

HIGHER SYMMETRIES IN JAHN-TELLER SYSTEMS

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To Mum
&
Dad (1917-1986)

Abstract

This thesis provides primarily a full and frank review of the many roles the $SO(3)$ algebra of quasispin has to play in nuclear, atomic and ligand-field theory. It is shown that the intriguing conclusion drawn by Ceulemans in 1984, i.e. that first order Jahn-Teller activity is forbidden in half-filled shell states, is directly related to the particularly simple expressions for the quasispin character of the half-filled shells, and also of the single-particle irreducible-tensor operators responsible for such activity.

The process of making transparent the relationships between the disparate formalisms used to derive selection rules for half-filled shell states involves the definition of a new antiunitary particle-hole conjugation operator with well defined properties and effects with respect to second quantized operators. It is also shown that this new operator is equivalent to the one used by Ceulemans in 1984.

Other “higher” symmetries in Jahn-Teller systems are the subject of discussion in Chapter 5, where a first attempt is made at merging the formalisms of supersymmetry and of para-bose statistics in $E \times e$ Jahn-Teller Hamiltonians.

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Chapter 1

Introduction

1.1 A brief history of quasispin

Seniority (and in its later incarnation quasispin) has found application in some quite disparate fields of physics. Racah [44] originally introduced the concept of seniority in order to tackle problems in complex spectra. It has since found application in the areas of nuclear and atomic science, generalised group theory, superconductivity, and ligand field theory.

In 1935 with their application of vector-coupling formulas to the problem of atomic spectra, Condon & Shortley [16] in the volume “Theory of Atomic Spectra” (henceforth referred to as TAS — as Racah) finally put previous empirical rules and special cases on a sound mathematical footing, and by introducing the concept of parentage they provided the necessary framework for the consideration of multi particle configurations.

Racah’s series of papers [42, 43, 44, 45] entitled “Theory of Complex Spectra” (henceforth TCS I–IV) over the period of time 1942 to 1949, enormously simplified the job of the atomic spectroscopists. While Condon & Shortley had detailed the methods of vector coupling in Chapter 3 of TAS, they had not applied it to the cases of complex spectra. In dealing with the coupling of two or more s , p or d electrons the numerical methods of Slater were still used in order to calculate the coefficients of certain integrals. Each case had to be dealt with on its own merits,

making generalisations extremely difficult. What was even worse, this method did not provide a way of separating identical terms.

The genius of Racah in TCS I was to be able to obtain these coefficients in a far more general manner using nothing more than the ordinary methods of matrix calculation. Rather than dealing with lengthy calculations for special cases he gave a closed formula for all. This had the effect of not only speeding up calculations of the electrostatic interaction between two electrons but also of providing the groundwork needed to handle terms involving three or more electrons.

Within a year of publication of TCS I Racah published again. In this classic paper TCS II where again he explored the spectra of two-electron configurations, Racah constructed the framework that would become modern spectroscopic physics. The concept of “Spherical tensor operators” was introduced, and the coefficients of Slater’s integrals were expressed as (sums of) scalar products of these. (The general formulae obtained in TCS I via (*LS*) coupling were shown to be derivable from this new method.) This method was extended to the cases of *jj*- and of *jl*-coupling, which were far more amenable for calculation of the spectra of many electron systems.

Refining the technique of fractional parentage coefficients (cfp) that had just been recently introduced by Goudsmit & Bacher [20], Racah extended his previous matrix methods to many-electron configurations in TCS III. It is in this paper that Racah first introduced the “seniority number” concept. Thus he was able to classify completely all terms arising from the configurations p^n and d^n .

The cfp for the configuration f^n did not come easily from Racah’s previous methods. Terms of the same kind were not able to be completely distinguished by them. As Racah points out in TCS IV, “(the method) for the configuration f^n (is) too cumbersome for practical use.” Racah looked for and found a solution in group theory. He discovered that the group G_2 (Cartan’s exceptional group), being a subgroup of R_7 and itself containing the group R_3 was exactly the group needed to provide irreducible representations with enough information to fully classify

the configuration f^n .

Spurred and aided by the success of Racah's methods in the classification of the states of atomic configurations, by 1952 the states of the p^n , d^n and f^n nuclear configurations were completely classified.

Realising the growing importance of the jj -coupling scheme, especially for the heavier nuclei, Flowers [19] investigated jj -coupling for many equivalent nucleon states. He arrived at a definition of seniority for this case which was equivalent to that which Racah developed for the LS (Russel-Saunders) coupling scheme. He did this by replacing spin with isospin, purely orbital functions by "spin orbital" functions, and proper orthogonal groups by symplectic groups.

The concept of "Complementary Shell States" was introduced in 1959 by Bell [4]. A complementary state was defined via the use of the particle-hole conjugation operator C which, as its name suggests, effectively swapped particle states with holes. As Bell comments, this paper is essentially a reconstruction in the language of second quantization of the ideas of Racah [42]. The most important of these being selection rules for half-filled shell states.

In 1961 Helmers [25] extended the work of Flowers by introducing the operators:

$$\begin{aligned} q_j &= \sum_m (-)^{j-m} a_{-m} a_m, \\ q_j^\dagger &= \sum_m (-)^{j-m} a_m^\dagger a_{-m}^\dagger, \\ p_j &= \sum_m (-)^{j-m} a_m^\dagger a_m^\dagger - \frac{1}{2}(2j+1), \end{aligned}$$

which he simply referred to as "bilinear symplectic invariants" bilinear in the annihilation and creation operators, symplectic because they commute with all operators of the symplectic group $USp(2j+1)$ introduced by Flowers for his classification scheme.

It is understood that the operators q, q^\dagger, p are defined in the space r_0 spanned by the basis

states,

$$|0\rangle, a_m^\dagger|0\rangle, a_{m_1}^\dagger a_{m_2}^\dagger|0\rangle, a_{m_1}^\dagger a_{m_2}^\dagger a_{m_3}^\dagger|0\rangle, \dots,$$

and a_m^\dagger, a_m are a hermitian conjugate pair of creation and annihilation operators, respectively, associated with the $2j + 1$ single-particle states

$$\psi_m(\mathbf{r}, \sigma), (m = -j, \dots, j - 1, j),$$

of a nuclear shell with half odd integer angular momentum j , m being the magnetic quantum number, \mathbf{r} the position and σ the spin variable.

Helmers noted that it was

remarkable (and indeed initiated the present investigation) that the three operators satisfy the same commutation relations as the spherical angular momentum operators i.e.

$$[q^\dagger, q] = 4p, [q, p] = 2q, [q^\dagger, p] = -2q^\dagger.$$

Kerman [35] was interested in the effect of “pairing forces” in describing nuclei which were rotating or vibrating or highly deformed. This two-particle force would move a pair of particles from any single-particle state to any other, and given the right conditions the matrix elements of it were quite significant.

Kerman discussed a restriction to the pairing force, in which N identical particles are all in the same level j^N . In this case the pairing force simply becomes Racah’s seniority force.

Apparently quite unaware of Helmers’ earlier work, Kerman defined the following three op-

erators¹ based on the usual annihilation and creation operators a_m, a_m^\dagger for each substate m :

$$\begin{aligned} s_+^m &= (-1)^{j+m} a_m^+ a_{-m}^+, \\ s_-^m &= (-1)^{j+m} a_{-m} a_m, \\ s_0^m &= \frac{1}{2} (a_m^+ a_m + a_{-m}^+ a_{-m} - 1), \end{aligned}$$

and showed, like Helmers, that

$$[s_+^m, s_-^m] = 2s_0^m, [s_0^m, s_+^m] = s_+^m, [s_0^m, s_-^m] = -s_-^m.$$

i.e. these operators have the same commutation relations as angular momentum. Bearing this in mind Kerman dubbed this triad of operators the *quasi-spin* \underline{s}^m corresponding to the level m and the sum

$$\underline{S} = \sum_{m>0} \underline{s}^m.$$

defines the total quasi-spin vector for this N particle level $(j)^N$

With reference to the works of Helmers and of Kerman, in their 1964 paper Lawson & MacFarlane [38] showed that the use of the Wigner Eckart theorem in quasi-spin space gave explicit formulae for the n dependence of matrix elements in shell model calculations for j^n . In doing so they laid the ground work in concept and notation for almost all further work in the field.

It is perhaps interesting to note that Watanabe's first paper [61] on the subject appeared almost coincidentally with that of Lawson & MacFarlane. This is acknowledged by Lawson & MacFarlane but they emphasise the originality of their work.

Watanabe, drawing directly on the work of Racah and of Bell in addition defines "Kramers Pair Operators" (which are obviously variants of quasispin operators), and examines the matrix relations for single and two electron scalar operators. He also reworks Bell's concept of complementary states and the linear complementary operator C in terms of these pair operators.

¹Where by convention the operators are not labelled by j as it is understood the author restricts himself to the j shell.

Through looking at the C transformation and the ensuing matrix relations between complementary states Watanabe arrives at his “Theorems for Half Filled Shells”.

In chapter seven of his terse volume² “Second Quantization and Atomic Spectroscopy” Judd [29] begins with a definition of quasispin operators and moves very quickly to point out the equivalence between quasispin and seniority (he seems to be the first to notice this). As Judd says,

The great advantage of the quasispin formalism over that of seniority is that various states and operators can be examined for their quasispin character by using the familiar rules for dealing with tensor operators.

After pointing out that quasispin commutes with the orbital and spin angular momentum vectors Judd shows how to construct a triple tensor, and using this concept he quickly runs through their algebra and demonstrates the analogy between the many-electron coupling properties of spin operators and of quasispin operators.

Judd postulates the existence of a conjugation operator C which effectively reverses the direction of the quasispin vector operator. It was chosen to be antilinear which made it behave analogously to the time reversal operator with respect to spin.

In discussing the special case of the half-filled shell Judd re-derives selection rules in a much more transparent way than Racah originally did.

Stedman [56] pushed further the work of Judd i.e. expressing the algebra of Quasispin in terms of Judd’s triple tensors. He seems to have been the first to formalise the explicit link between the particle-hole conjugation operator C and quasispin in that he gave a representation of C in terms of the cartesian components of quasispin. The emphasis of this paper is on the abstract algebra (commutation relations) of quasispin and to forge a much more complete

²A transcription of Judd’s seminars at the Dieke Memorial lectures

analogy with time reversal than Judd did, and so to get analogues to time reversal selection rules.

In addition, however, Stedman attempts to generalize Judd’s development using an original notation and making as few assumptions as possible, in order that the results not be applicable merely to $SO(3)$ symmetry (as in Judd) but also, say, to point groups or other instances of reduced symmetry. In §4.2.2 of this thesis Stedman’s development is examined. Unfortunately it is found that the incorporation of antilinearity in the particle-hole conjugation operator as outlined in Stedman’s paper (Stedman [56]) produces inconsistencies unresolvable with the desire to maintain generality. In fact, some of the properties of Stedman’s antilinear particle-hole conjugation operator as listed in Stedman [56] are found to be in error.

These inconsistencies draw attention to one of the main points of discussion of this thesis: should a linear or an antilinear particle-hole conjugation operator be used, or are both useful?

The answer to this question is perhaps best provided by an examination of the 1984 paper of Ceulemans (Ceulemans [12]) who, in the context of an examination of the symmetries possible in the theory of molecular ligands, develops an antiunitary “complementarity” (particle-hole conjugation) operator, which he denotes $O(\varphi)$. It is discovered in §4.3.4 that the antilinear $O(\varphi)$ is related to a linear particle-hole conjugation operator C_L via the relationship $O(\varphi) = C_L O(\theta)$, where $O(\theta)$ is the time reversal operator of Wigner. Using this operator Ceulemans derives selection rules for half-filled ligand shells which are found to have profound implications on the Jahn-Teller activity of the ligand.

The next introductory section discusses the history and development of the theory of Jahn-Teller activity.

1.2 The Jahn-Teller effect

In a historical note before the preface of Englman’s treatise [17] on vibronic interactions and the Jahn-Teller effect Edward Teller suggests that the effect should carry the name of Lev Landau,

for it was he who suspected the effect and no one, claims Teller, has given a proof that a mathematician might enjoy. “Jahn and I merely did a bit of spade work” he concludes.

In this spirit I suggest that the effect not carry the name of the mighty Landau, who is not lacking recognition in many areas of mathematics and physics³, but instead that of a student of Teller’s R. Renner, whose Ph.D. thesis gave Teller the ammunition to win an argument with Landau (a rare occurrence, according to Teller) and who after World War 2 left the area of physics to embark on a career in weather prediction (“another casualty of the war”, in Teller’s words). For if it had not been for Renner, Teller’s interest may never have been piqued enough to fully investigate the extent of the vibration-electronic interaction problem.

In 1936 Teller met Landau at the Copenhagen Institute of Niels Bohr and discussed the modes of vibration of CO₂. Landau was of the impression that (orbitally) degenerate electronic states in CO₂ (a linear molecule) would be unstable, i.e. would split with respect to some normal mode of vibration of the nuclei. It was at this stage that Teller informed Landau of the Ph.D. thesis of Renner concerning linear tri-atomic molecules, in which Renner had shown that in particular linear molecules would not exhibit such behaviour.

One year later in London Hans Jahn and Edward Teller (both fleeing German universities under Nazi control) collaborated on the paper “Stability of poly-atomic molecules in degenerate electronic states I. Orbital degeneracy” [26]. By an exhaustive method they proved the theorem which now bears their names. It is ironic that a theorem which gives rise to so many elegant examples of the role symmetry plays in physics — some of which will be examined in this thesis — should have to be proved by the thoroughly inelegant method of brute force⁴.

³Physical terms bearing Landau’s name are: Landau diamagnetism, Landau levels in solid-state physics, Landau damping in plasma physics, Landau energy spectrum in low temperature physics and Landau cuts in high-energy physics. In 1962 Landau won the Nobel prize in physics (for liquid Helium). All these are in addition to his swathe of Soviet awards and the naming of the Landau crater on the moon!

⁴Formal proofs have since been discovered — see for example [6, 49]

After the first announcement of the theorem, the Jahn-Teller effect was largely ignored for decades. It is very elusive to show experimentally, as it is an extremely subtle effect and requires the use of exceptionally delicate equipment and experimental techniques. Another reason for this lack of work in the Jahn-Teller area was a general misinterpretation of the expected observable effects. Experimentalists hunting for signs of literal physical deformations of ionic structures were quite disappointed in their quest. It is now generally accepted that in itself the Jahn-Teller theorem contains *no* information regarding magnitudes of observable effects. The correct interpretation of the Jahn-Teller theorem, as further discussed below, has to do with the intersection of various adiabatic potential sheets. More specifically, the fact that at or near the point of intersection (see Figure 1.1), these surfaces can no longer be given a physical interpretation. However what the Jahn-Teller theorem does provide is a system of coupled equations

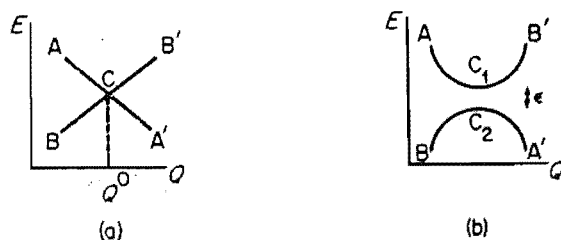


Figure 1.1: These figures show adiabatic sheets near/at the point of intersection (energy versus the vibrational coordinate Q).

(a) Intersection of two potential energy sheets. The cross-over point C is the point of degeneracy.

(b) Two potential energy sheets near degeneracy, separated by energy ϵ .

This is Figure 2.1 of Englman [17].

describing the dynamics of the nuclei which take into account non-adiabatic mixing of different electronic states. In general these equations describe effects far more wide ranging than simply instability of the nuclear configuration and removal of degeneracy of electronic states.

With the advent of more and more sophisticated techniques over the years the Jahn-Teller effect has begun to be much better understood. On the other hand a simple sentence or paragraph description of the Jahn-Teller effect has got harder to formulate. When Jahn and Teller first

approached the topic it was from the point of view of deviations from the Born-Oppenheimer approximation pertaining to degenerate electronic states in poly-atomic molecules. This point of view has changed and become more sophisticated over the years. The main development has been the use of the adiabatic approximation instead of the Born-Oppenheimer approximation. The Jahn-Teller theorem now is connected to the breakdown of the applicability of this approximation near the intersection of two or more adiabatic potential sheets, i.e. at a point of degeneracy.

The Born-Oppenheimer approximation takes advantage of the great discrepancy between the masses of nuclei and of electrons. Effectively the approximation assumes the spatial distribution of nuclei is constant, i.e. the nuclei are regarded as being fixed points. The electrons are then free to roam this structure. Vibrations of the nuclei are introduced as perturbations later.

The Jahn-Teller theorem examines the link between the spatial symmetry of the nuclei, the normal modes of vibration of these nuclei and the possible irreducible representations of the electronic states.

For the nuclear configuration to be a stable one, terms linear in the normal co-ordinates of the nuclei must vanish from the perturbation expansion.

If spin is ignored for the moment (removing the necessity to consider the degeneracy due to Time Reversal — Kramers' theorem) then the condition required for the configuration to be a stable one is for integrals of the form

$$\int \psi_{\rho}^* V_{\alpha i} \psi_{\sigma} dq,$$

to vanish, where $\psi_{\rho}, \psi_{\sigma}$ are wave functions of electronic states belonging to the same degenerate term and $V_{\alpha i}$ is an expansion coefficient of the perturbation with the important property that it transforms according to the same irreducible representation as does the corresponding normal co-ordinate $Q_{\alpha i}$. $V_{\alpha i}$ is a function of the electronic co-ordinates only.

If $\Gamma^{\rho}, \Gamma^{\sigma}$ refer to the irreducible representations of the symmetry group G of the Hamiltonian, by

which the wave functions ψ_ρ, ψ_σ transform respectively, and Γ^α to the irreducible representation by which $V_{\alpha i}$ (and also $Q_{\alpha i}$) transform, then by a simple application of the great orthogonality theorem of group theory the integral will vanish unless the direct product $\Gamma^{\rho*} \times \Gamma^\alpha \times \Gamma^\sigma$ contains the identity representation Γ^1 of G . Or, to put it another way, the direct product $\Gamma^\alpha \times \Gamma^\sigma$ contains Γ^ρ , i.e., the configuration will be unstable if the above criteria are met.

By an exhaustive examination of all 32 point groups Jahn and Teller verified that Γ^1 appears in all triple products except those for which the irreducible representations belong to the group G appropriate for a linear molecule.

The conclusion Jahn and Teller drew from this is now referred to as the Jahn-Teller theorem:

When there is a degenerate electron state, any symmetric position of the nuclei is unstable. As a result of this instability, the nuclei move in such a way that the symmetry is destroyed and the degeneracy of the term is removed.

There are two exceptions to this general statement. One is already touched upon above, the case of a linear molecule, the second being if the presence of spin is accounted for, then the Kramers' degeneracy which is allowed by this will not be removed.

Care needs to be taken, however, in interpreting exactly what this theorem is saying (O'Brien [40] and Judd [31]). Specifically the theorem does not explicitly say that distortion will occur, but simply that it is permitted to occur. Nor does it say that distortion will not occur in the cases when the integrals vanish, but rather that nothing can be concluded about stability of the configuration in this case (see Judd §3 for further details).

There are two reasons for inclusion of material referring to Jahn-Teller theory in this thesis. One is that, as is already described, the feature-rich nature of the so called Jahn-Teller Hamiltonians — Hamiltonians describing the vibronic system at the point of adiabatic breakdown. These

Hamiltonians are described by the author as feature rich as they provide examples of symmetries in physics more than those geometrical ones which provide their existence. In particular Chapter 5 discusses the possibility of Parabose Super-Symmetric Jahn-Teller Hamiltonians, which are Hamiltonians which exhibit mixing of boson and fermion degrees of freedom (super-symmetric) and yet also to some degree may be described in terms of parabosons (fermions coupled together in such a way as to exhibit bosonic properties).

Another reason for the consideration of Jahn-Teller theory is that in Chapter 4 selection rules will be developed for Jahn-Teller Hamiltonians described in terms of quasi-spin operators. Specifically it will be shown that isolated half-filled shell states cannot exhibit first-order Jahn-Teller activity.

Chapter 2

Parity and bipartite structures

It is felt by the author that this chapter, despite its smallness in physical size, is perhaps one of the most important chapters of this thesis. The techniques of creating bipartite algebraic expressions are essential to the understanding of the finding and correcting of errors in Stedman's 1997 paper (Stedman [56]), as outlined in §4.2.2. The usefulness of these techniques and rules are not merely limited to this one, specific case however. They are based on larger, more powerful sets of (diagram) rules and techniques in group theory and quantum mechanics. The 1990 book by Stedman "Diagram Techniques in Group Theory" [57] is taken to be the standard reference in this regard. It should be noted however, as mentioned by Stedman, that there are almost as many conventions, styles and phase choices as there are authors in this area.

One of the primary rules for constructing valid diagrams which express group theoretical or quantum mechanical ideas, is the notion of parity. The term "parity" is used here not in the more commonly used sense of the effect of time reversal or inversions on a quantum mechanical system¹, but more in the sense of "good housekeeping" (to use the phrase coined by Stedman) in constructing diagrams corresponding to meaningful physical expressions. As will be shown the concept of parity for valid quantum-mechanical expressions, is closely related to the fundamental fact of quantum mechanics, that any real, observable operator, (an operator with eigenvalues that may be experimentally measured) must be hermitian.

¹Although these are discussed in this thesis, and every effort to distinguish between them is made

A valid tensorial expression, say in relativity theory, has contraction of indices occurring (summing over identical indices) only between contravariant (raised) and covariant (lowered) indices. For example

$$g_{\mu\nu}T^{\nu}{}_{\kappa\lambda}. \quad (2.1)$$

The contraction is occurring here on the covariant and contravariant indices ν . This rule for contraction could equally well be stated “assign (arbitrarily) either a plus or a minus sign to contravariant indices. When that choice has been made, the opposite sign — minus or plus — is then assigned to the covariant indices. Contraction of indices can then only occur between indices of opposite sign (parity)”.

The convention used in Stedman [57] is to assign parity “+” to contravariant indices and parity “−” to covariant.

This convention for only contracting on indices of opposite parity is referred to as maintaining the “biparticity” of an expression.

The notion of a bipartite expression (and consequently of parity) need not be restricted to tensorial equations. Parity may also be assigned to the bras, kets and tensorial operators of quantum mechanics (amongst other things). Conventionally a ket is assigned parity “−” and a bra “+”. It is immediately obvious that the action of the hermitian conjugation operator (which takes a bra into a ket and vice-versa) reverses parity. This will be seen to be true for any antilinear operator — such as time reversal. It follows that the condition that any operator, \underline{A} , corresponding to a real, observable eigenvalue, a , must be hermitian (equal to its own hermitian conjugate) implies that \underline{A} must have no net parity, i.e. the parity of \underline{A} is 0 (this is a necessary condition, but not a sufficient one since there exist operators with nil net parity which are not hermitian).

Since a ket, $|K\rangle$ say, has negative parity, so then must its second quantized equivalent, the

creation operator a_K^\dagger , where

$$a_K^\dagger|0\rangle \equiv |K\rangle. \quad (2.2)$$

It follows that the annihilation operator a_K must be of positive parity. An argument therefore could be made for writing the annihilation operator as a^K , the label raised as for a contravariant tensor label. For simplicity's sake this shall not be done. However when the need to emphasise the parities of labels (or of operators corresponding to those labels) does arise, this shall be done by placing the appropriate sign over the label (or operator). For example the definition of a number operator for state $|K\rangle$ could be written

$$n(K) = a_K^\dagger a_K, \quad (2.3)$$

where the negative sign over the creation operator is not to be confused with the time-reversal operator which is frequently denoted by an overbar on the operator; e.g. $Ta_K^\dagger T^{-1} = \bar{a}_K^\dagger$. The other important thing to note here is that as n has no net parity it must be written in such a way that it has no indices, e.g. as $n(K)$.

The $2jm$ symbol (KL) couples two operators transforming as irreducible representations K and L of some group G to an invariant of that group (for more information on the $2jm$ and $3jm$ symbols see Appendix A). Since the ket $|K\rangle$ transforms as the irreducible representation K , the creation operator a_K^\dagger is an irreducible tensor operator also transforming as the irreducible representation K . It has previously been mentioned that a_K^\dagger has negative parity, and it is obvious that an invariant, having no labels, can have no net parity. Therefore each label on the $2jm$ must have positive parity — (KL) — and an expression such as $(KL)a_K^\dagger a_L^\dagger$ has no net parity (the parities sum to zero) as is befitting of an invariant.

Hermitian conjugation, as mentioned above, reverses parity, it is also an example of an antilinear operator (hermitian conjugation, commonly represented by the dagger symbol \dagger , conjugates complex numbers). An argument may therefore be constructed to deduce the effects of complex

conjugation on parity,

$$\begin{array}{ccc} + & + & - & - \\ \left((KL) a_K^\dagger a_L^\dagger \right)^\dagger & = & (KL)^* a_L a_K. \end{array} \quad (2.4)$$

The net parity on the left-hand side of the above equation is 0, and must of necessity remain so after hermitian conjugation. The parity of the labels of the complex conjugated $2jm$ symbol therefore must be negative, i.e.

$$\begin{array}{ccc} + & + & - & - \\ (KL) & \text{complex conjugation} & (KL)^*. \end{array} \quad (2.5)$$

Complex conjugation reverses the parity of labels, as must any antilinear operator. Conversely any linear operation must preserve parity.

Other examples of parity conserving operations are the quantum-mechanical commutator and anticommutator, e.g.

$$\begin{array}{ccc} - & - & + & - \\ \left[a_K^\dagger a_L^\dagger, a_L a_L^\dagger \right] & = & a_K^\dagger a_L^\dagger, \end{array} \quad (2.6)$$

where the square brackets, as is common, denote the commutator. The net parity is the same on the left as it is on the right. If this were not so an error would be indicated in the few lines of working taken to achieve this result.

This “net absolute parity” rule is similar in nature to what Stedman refers to as “good house-keeping”. Stedman’s “housekeeping” is the whole idea of biparticity. As previously mentioned this is the rule that labels of parity “+” must always be contracted with labels of parity “−”. For example the expression

$$\begin{array}{ccc} + & + & - \\ (KL) a_L^\dagger \end{array} \quad (2.7)$$

is correct, unlike the expression

$$\begin{array}{ccc} - & - & - \\ (KL)^* a_L^\dagger \end{array} \quad (2.8)$$

which is not bipartite.

Equation (2.5) provides another interesting result. In cases where the $2jm$ symbol is real (e.g. in $SO(3)$ symmetry) the parity of the labels must either be 0 or, as complex conjugation in this case has no effect, must be arbitrarily chosen to be either of positive or of negative parity. The convention used in this thesis is to maintain the parity of real $2jm$ labels as +.

Chapter 3

Quasispin in spherically symmetric fields ($SO(3)$)

This chapter is intended to be an introduction to the next, in which situations of reduced spatial symmetry, e.g. ligand-field theory, will be encountered.

As in many other areas of interest in physics the concepts of quasispin, seniority and particle-hole conjugation in situations of complete spherical symmetry are well understood ones and well suited as simple introductions to more complex cases. The introduction to such matters from a $SO(3)$ point of view is doubly apt, as most of the development of quasispin was carried out by workers in the fields of nuclear shell theory and also atomic shell theory. Both cases, of course, being subject to the prevailing $SO(3)$ symmetry of the sphere. There are subtle differences between these two cases (nuclear and atomic shell theory) however. Because of the high energy involved in nuclear shell theory the spin and orbital angular momenta are strongly coupled to total angular momenta which is labelled j . Interactions between equivalent particles are then best discussed using the jj -coupling scheme.

In atomic shell theory, on the other hand, the prevailing coupling scheme of two or more equivalent (degenerate) electrons is the Russell-Saunders scheme, otherwise known as the LS-coupling scheme.

Therefore matters of particle-hole conjugation and quasispin in the jj -coupling scheme are discussed in §3.1, whilst in §3.2 the point of view from the LS-coupling scheme is examined. This leads to Judd's [29] definition of a "triple tensor" in §3.2.3.1.

The chapter closes with an examination of the commutation relations of the components of quasispin with Judd's antilinear particle-hole conjugation operator. As will be seen in §4.2 it was this operator that Stedman [56] chose to generalize to cases of reduced symmetry.

While the main purpose of this chapter is to serve as a detailed review of the background of quasispin and related matters in $SO(3)$ symmetry, there exists a hint of original work in §3.1.6. The derivation of these selection rules for $SO(3)$ symmetry by this methodology (which, as will be seen in §4.3.8 is based on that of Ceulemans [12] for the case of ligand fields) to the authors' knowledge, has not been seen in the literature before. However, as also will be seen in §4.3.9 they do turn out to be closely related to rules given by Wybourne [67] and, interestingly, Ceulemans in another, later paper [13].

As previously stated this section (and indeed the bulk of this thesis) is devoted to three closely linked fields of study: particle-hole conjugation, seniority and quasispin. It turns out that each is simply a visible facet of an underlying symmetry and to understand the problem as a whole each must be examined in turn. Particle-hole conjugation is perhaps the easiest to understand conceptually of the three, so it will make a good starting point in §3.1.2.

In the following description of particle-hole conjugation the relevant equations will be expressed in terms of second quantised operators satisfying

$$\{a_{jm}, a_{jn}^\dagger\} = \delta_{mn}, \quad (3.1)$$

$$\{a_{jm}, a_{jn}\} = \{a_{jm}^\dagger, a_{jn}^\dagger\} = 0. \quad (3.2)$$

Particle-hole conjugation may be the easiest concept to grasp, but quasispin expresses the un-

derlying symmetry most succinctly. Historically seniority was the most influential aspect, vital to the work of Racah [45] and the many others who followed in his giant footsteps.

3.1 The jj -coupling scheme

Again for simplicity's sake, in this introductory section Bell's [4] definition of a particle-hole conjugation operator will be followed and attention has been restricted to the j shell. In addition, in this development of particle-hole conjugation jj -coupling is used for simplicity. This is adequate to highlight the form of the equations and to link in with the work of the other nuclear scientists who were so influential in the 50s in pushing forward the concepts of particle-hole conjugation and quasispin. Later the triple tensor methods of Judd (Judd [32, 29]) will be looked at, who being an atomic spectroscopist uses the LS-coupling (Russell-Saunders) scheme in his development. The transition from jj - to LS-coupling with respect to particle-hole conjugation will be made in a formal way.

3.1.1 Particle-hole conjugation defined

The concept of particle-hole conjugation relies for its definition upon the idea of a closed shell, where "closed shell" means any configuration which is invariant under the actions of the relevant symmetry group. For example an isolated atom, with no external fields acting upon it, has spherical symmetry i.e. it is invariant under the actions of the group $SO(3)$. A shell in this instance refers to the $(2j + 1)$ degenerate states corresponding to the same quantum numbers j and distinguished by the label m_j where $-j \leq m_j \leq j$, $m_j = j, j - 1 \dots j$.

When defining the concept of a hole the nature of the filled shell must first be known. In this case it is used to indicate the absence of a particle in a filled shell — a vacant state.

There is physical evidence to indicate there is some similarities between shells with N particles in their shells and those with $(2j + 1) - N$ i.e. between states for which N particles have been "exchanged" for N holes. The mathematical relationship between matrix elements of less than half-filled shells and those of greater than half-filled shells will be shown later. In the past

this has greatly eased calculations.

3.1.2 Equations for particle-hole conjugation

It will prove useful to define the symmetry-adapted annihilation operator $\tilde{a}_{jm} \equiv (-1)^{j-m} a_{j-m}$ which transforms under rotations in the same way as does its creation operator partner a_{jm}^\dagger . In other words, \tilde{a}_{jm} has the same commutation relations with the angular momentum operators as does a_{jm}^\dagger .

This can best be shown by considering the second quantized form of the angular-momentum operators

$$\hat{J}_+ = \sum_{mn} a_{jm}^\dagger \langle jm | \hat{J}_+ | jn \rangle a_{jn} \quad (3.3)$$

$$\hat{J}_- = \sum_{mn} a_{jm}^\dagger \langle jm | \hat{J}_- | jn \rangle a_{jn} \quad (3.4)$$

$$\hat{J}_0 = \sum_{mn} a_{jm}^\dagger \langle jm | \hat{J}_0 | jn \rangle a_{jn}. \quad (3.5)$$

With these definitions the relations

$$[\hat{J}_+, a_{jm}^\dagger] = \sqrt{j(j+1) - m(m+1)} a_{jm+1}^\dagger \quad (3.6)$$

$$[\hat{J}_-, a_{jm}^\dagger] = \sqrt{j(j+1) - m(m-1)} a_{jm-1}^\dagger \quad (3.7)$$

$$[\hat{J}_0, a_{jm}^\dagger] = m a_{jm}^\dagger \quad (3.8)$$

may easily be shown. These indicate that a_{jm}^\dagger transforms under rotations as a tensor of rank j (see Racah [43]).

However for the annihilation operator a_{jm} to satisfy the above commutation relations it will quickly be seen that the transformation

$$a_{jm} \rightarrow \tilde{a}_{jm} = (-1)^{-m} \delta_{m-m} a_{jm} = (-1)^{j-m} a_{j-m} \quad (3.9)$$

is first required¹.

¹It will be recognised that $(-1)^{j-m} \delta_{m-m}$ is the $2j$ symbol for the group $SO(3)$

If the empty shell is given by the ket $|0\rangle$, the particle-hole conjugation operator is defined, here following Bell, to be the linear operator C that has the following properties:

$$C|0\rangle = \prod_{m=-j}^j a_{jm}^\dagger |0\rangle \equiv a_{jj}^\dagger a_{jj-1}^\dagger \dots a_{j-j}^\dagger |0\rangle \quad (3.10)$$

$$C|a\rangle = C a_{jm}^\dagger a_{jn}^\dagger \dots |0\rangle = \tilde{a}_{jm} \tilde{a}_{jn} \dots C|0\rangle = |b\rangle \quad (3.11)$$

for any number of (different) creation operators. It should be noted that the order of creation operators in the product in equation (3.10) is vital.

The filled shell $C|0\rangle$ is a rotational invariant and, as has been shown above, a_{jm}^\dagger and \tilde{a}_{jm} transform similarly under rotation. This proves that $|b\rangle$, the particle-hole conjugate state to $|a\rangle$, rotates the same way as $|a\rangle$, or to put it another way the particle-hole conjugation operator C commutes with angular momentum, $[C, \underline{J}] = 0$.

Another important property of C can be deduced by noting that C takes one ortho-normal set of operators and transforms them into another. Hence, according to the definition of Bell, C is a unitary operator

$$C^{-1} = C^\dagger. \quad (3.12)$$

Further properties of C are apparent from the following equations:

$$C a_{jm}^\dagger C^{-1} = \tilde{a}_{jm} = (-1)^{j-m} a_{j-m} \quad (3.13)$$

$$C a_{jm} C^{-1} = \tilde{a}_{jm}^\dagger = (-1)^{j-m} a_{j-m}^\dagger. \quad (3.14)$$

It follows that

$$C^2 a_{jm}^\dagger C^{-2} = (-1)^{2j} a_{jm}^\dagger \quad (3.15)$$

and, by considering the action of C^2 on the empty shell that

$$C^2 |0\rangle = (-1)^{j(2j+1)} |0\rangle. \quad (3.16)$$

Therefore for an arbitrary shell $|a\rangle$ with a configuration of N particles, the action of C^2 is

$$C^2 |a\rangle = C^2 a_{jm}^\dagger a_{jn}^\dagger \dots |0\rangle = (-1)^{j(2j+1+2N)} |a\rangle \quad (3.17)$$

$$\text{i.e. } C^2 = (-1)^{j(2j+1+2N)} = (-1)^{j(2j+1-2N)}. \quad (3.18)$$

The last equality follows because $2j$ is integral and N , the number of particles in the shell, is also integral.

In the special case of the half-filled shell, i.e. when $2N = 2j + 1$, it can be seen from equation (3.18) that the eigenvalue of C^2 is 1. Hence the eigenvalue of C must be ± 1 . Therefore the action of C upon a half-filled shell state is to create another half-filled shell state and there must exist two types of half-filled shell states with definite parity with respect to the operator C . This fact has been noted in the past by, for example, Griffith (Griffith [23] page 247) who arrived at this result by quite a different route and in quite a different physical situation.

The concept of particle-hole conjugation is not restricted to free atoms or ions in spherically symmetric surroundings. Griffith, for example, discusses the topic of holes and particles in the t_2^n configuration of the d orbitals in the case of a strongly coupled octahedral crystal field. This general situation will be discussed at length in the next chapter. Particular attention will be paid to instances of half-filled ligand shells, for as shall be shown, powerful selection rules may be derived from these “auto-complementary” states.

3.1.3 Matrix elements of single particle operators

In this section a relationship will be developed between matrix elements of a single-particle tensor operator of rank k , $T_q^{(k)}$, and matrix elements of $T_q^{(k)}$ evaluated between states complementary to the original ones. That is the connection between

$$\langle b | T_q^{(k)} | a \rangle \quad \text{and} \quad \langle b' | T_q^{(k)} | a' \rangle, \quad (3.19)$$

where $|a'\rangle = C|a\rangle$ and $|b'\rangle = C|b\rangle$, will be examined.

The second-quantized form of a single-particle tensor operator is

$$T_q^{(k)} = \sum_{mn} a_{jm}^\dagger \langle jm | T_q^{(k)} | jn \rangle a_{jn} \quad (3.20)$$

$$= \sum_{mn} a_{jm}^\dagger t_{mn}^q a_{jn}. \quad (3.21)$$

Hence

$$\langle b' | T_q^{(k)} | a' \rangle = \langle b | C^\dagger T_q^{(k)} C | a \rangle. \quad (3.22)$$

The following will now be used: the unitary property of C , its action on the annihilation and creation operators for the j shell (see equations (3.13) and (3.14)), the fact that one of the consequences of the Wigner-Eckart theorem for SO(3) is that $m - n$ must equal q for t_{mn}^q not to vanish, and lastly $(-1)^{j-m} = (-1)^{m-j}$. Hence

$$C^\dagger T_q^{(k)} C = C^{-1} T_q^{(k)} C \quad (3.23)$$

$$= C^{-1} \left(\sum_{mn} a_{jm}^\dagger t_{mn}^q a_{jn} \right) C \quad (3.24)$$

$$= \sum_{mn} (C^{-1} a_{jm}^\dagger C) (C^{-1} t_{mn}^q C) (C^{-1} a_{jn} C) \quad (3.25)$$

$$= \sum_{mn} (-1)^{j-m} a_{j-m} t_{mn}^q (-1)^{j-n} a_{j-n}^\dagger \quad (3.26)$$

$$= (-1)^q \sum_{mn} t_{mn}^q a_{j-m} a_{j-n}^\dagger. \quad (3.27)$$

The anti-commutation relations of the annihilation and creation operators are now used to give the expectation value of $T_q^{(k)}$ i.e. t_{mn}^q , in one open-shell configuration, in terms of the expectation value in the closed shell, and the expectation value in the complementary shell.

$$C^\dagger T_q^{(k)} C = (-1)^q \left\{ \sum_m t_{mm}^q - \sum_{mn} t_{-n-m}^q a_{jm}^\dagger a_{jn} \right\}, \quad (3.28)$$

where the substitution $m \rightarrow -n$ has been employed in the second summation term on the left — note that this maintains the identity $q = m - n$.

Again the Wigner-Eckart theorem is useful. The first term, $\sum_m t_{mm}^q$ — being the expectation value of $T_q^{(k)}$ in the closed shell — must necessarily vanish if T is not a scalar, i.e., if $k \neq 0$. Also the theorem states that for a given j and k the matrix elements t_{mn}^q are proportional to the Clebsch-Gordan Coefficient:

$$\langle kqjn | kjjm \rangle \quad (3.29)$$

which has the following symmetry property²

$$\langle kqjn|kjjm\rangle = (-1)^{k+j-j}\langle k-qj-n|kjj-m\rangle \quad (3.30)$$

$$= (-1)^k\langle k-qj-n|kjj-m\rangle. \quad (3.31)$$

This is a consequence of the Derome-Sharp lemma restricted to $SO(3)$, see Butler [9] page 57, Hence

$$(-1)^qt_{-n-m}^q = (-1)^k((-1)^qt_{nm}^{-q}) \quad (3.32)$$

$$= (-1)^k\{t_{mn}^{\dagger q}\}^* \quad (3.33)$$

where $t_{mn}^{\dagger q}$ is the q component of the Racah Conjugate Tensor (see Racah [43] equation (25))

$$(t_{mn}^q)^\dagger = (-1)^q(t_{mn}^{-q})^*. \quad (3.34)$$

In summary

$$\langle b'|T_q^{(k)}|a'\rangle = \langle b|C^{-1}T_q^{(k)}C|a\rangle, \quad (3.35)$$

$$= \langle b|\{\langle c|T_q^{(k)}|c\rangle - \sum_{mn}(-1)^k\{t_{mn}^{\dagger q}\}^*a_{jm}^\dagger a_{jn}\}|a\rangle, \quad (3.36)$$

$$= \langle b|a\rangle\langle c|T_q^{(k)}|c\rangle - (-1)^k\langle b|T_q^{(k)\dagger}|a\rangle^*, \quad (3.37)$$

where the filled shell is represented by the ket vector $|c\rangle$, and use has been made of the fact that with appropriate phase conventions, states such as $|a\rangle$ and $|b\rangle$ can be built up by sums of products of the creation operators with real coefficients, thus allowing the complex conjugation to be taken outside.

²See property (4c) in Appendix A.3.1

Columns in which both the upper and the lower cells are shaded represent two states which are coupled to a rotational invariant, i.e. the two states are combined in such a way as to not affect the net total angular momentum of the configuration. In this respect shaded columns are equivalent to those unshaded. Only those shaded cells which are alone in their column need be considered when ascertaining the transformation properties of the configuration. However it should be noted that conclusions about transformation properties of states depicted by these diagrams can only be made in cases of spherical symmetry, for it is only in this case that the labels j and m , labelling as they do the irreducible representations $SO(3)$ and $SO(2)$, completely describe the transformation of the state³.

Ignoring at this stage, for the sake of clarity, such niceties as coupling coefficients and phase factors⁴, the occupancy of the state represented by figure 3.2 corresponds to that of the following, second-quantized expression

$$|a\rangle = a_{\frac{13}{2} \frac{13}{2}}^\dagger a_{\frac{13}{2} \frac{7}{2}}^\dagger a_{\frac{13}{2} \frac{5}{2}}^\dagger a_{\frac{13}{2} \frac{1}{2}}^\dagger a_{\frac{13}{2} \frac{-5}{2}}^\dagger a_{\frac{13}{2} \frac{-9}{2}}^\dagger a_{\frac{13}{2} \frac{-11}{2}}^\dagger |0\rangle. \quad (3.38)$$

If the particle-hole conjugation operator C is allowed to act upon this configuration the occupancy changes to that corresponding to the following expression (bearing in mind the same caveats discussed above about coupling coefficients etc.)

$$|b\rangle = C|a\rangle = a_{\frac{13}{2} \frac{13}{2}}^\dagger a_{\frac{13}{2} \frac{7}{2}}^\dagger a_{\frac{13}{2} \frac{3}{2}}^\dagger a_{\frac{13}{2} \frac{1}{2}}^\dagger a_{\frac{13}{2} \frac{-3}{2}}^\dagger a_{\frac{13}{2} \frac{-9}{2}}^\dagger a_{\frac{13}{2} \frac{-11}{2}}^\dagger |0\rangle. \quad (3.39)$$

In terms of diagrams the action of C upon $|a\rangle$ to produce $|b\rangle$ is given in Figure 3.3. From this diagram the action of C can clearly be seen. It has the effect of removing “zero-coupled” states — two states which are coupled together to have nil net angular momentum — and of adding zero-coupled states in such a way as to not disturb un-coupled states. This is represented by shading those columns which are unshaded, and unshading those columns which were originally

³The mnemonic is open to generalization, however, if each cell is labelled by a composite label K (see Appendix A) and it situated in the same column as its conjugate state labelled \bar{K}

⁴not to mention biparticity, as discussed in Chapter 2!

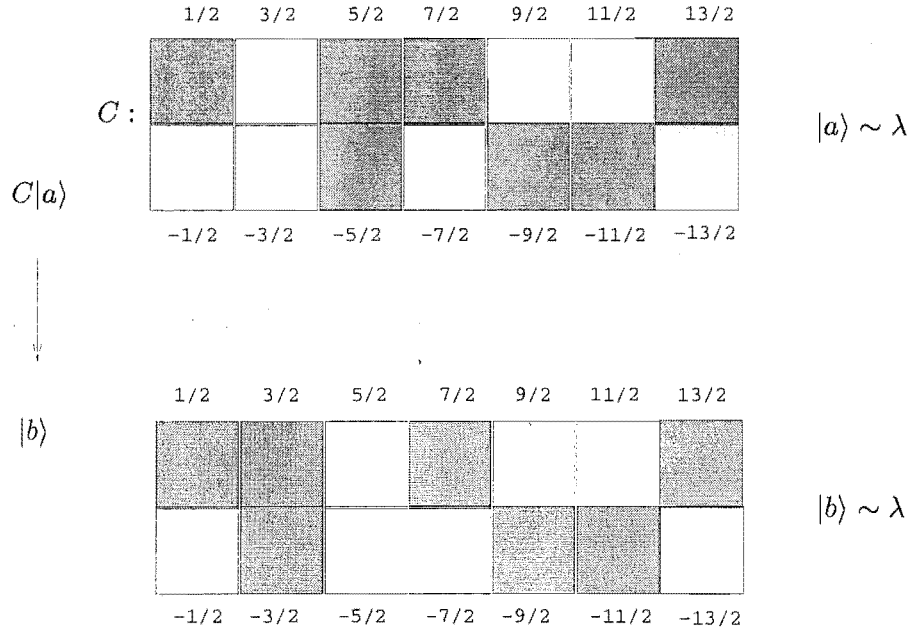


Figure 3.3: These states transform the same way under rotations, i.e. must belong to the same or equivalent irreducible representations of the symmetry group $SO(3)$. The operator C was chosen in this way so as to preserve the seniority ν (or equivalently, the quasispin Q).

shaded, leaving all other cells untouched.

Because $|b\rangle$ has been obtained from $|a\rangle$ via the addition or deletion of zero-coupled states, $|b\rangle$ must belong to the same or equivalent irreducible representations of the symmetry group (which is in this case $SO(3)$).

The operator C was defined with this in mind. As will be shown in later sections, this is intimately related to the notions of seniority (roughly equivalent to the number of unpaired cells) and quasispin (roughly equivalent to the number of zero-coupled states).

It should be noted that in $SO(3)$ all irreducible representations are real and $\lambda \sim \lambda^*$. Hence the operator C could very well have been chosen to be anti-unitary (i.e. antilinear and unitary). The relative merits of choosing C to be linear or antilinear will be discussed in more detail

(particularly in reference to quasispin) in §3.2.4 and further in §4.2.2.6.

As mentioned above, so far in this section the particle-hole conjugation operator has been one chosen not to affect the rotational properties of the state which it acts upon, i.e. C commutes with total angular momentum. At this point it seems apt to mention another equally valid choice for a particle-hole conjugation operator.

Ceulemans (see Ceulemans [12]) chose as his particle-hole conjugation operator one which simply replaced every occupied state with an un-occupied one and vice-versa (see Figure 3.4). As will be shown in the next chapter this operator, $O(\varphi)$, takes the state $|a\rangle$ transforming as the irreducible representation λ , to the state $|b\rangle$ which transforms as λ^* , so that the original state $|a\rangle$ and conjugate $|b\rangle$ couple to an invariant, i.e. the closed shell. With this definition of the particle-hole conjugation operator $O(\varphi)$, it is immediately seen that $O(\varphi)$ must be anti-unitary — which, as will be seen shortly, is similar in nature to the time reversal operator T .

All this is trivial in $SO(3)$ as the complex conjugate irreducible representation λ^* is equivalent via a unitary transformation (the $2jm$ matrix $(-1)^{j-m}\delta_{m-m}$) to λ . It does mean, however, that the states $|b\rangle$ in Figures 3.4 and 3.3 are equivalent. That is the actions of C and of $O(\varphi)$ are the same.

The operation of time reversal is given the definition in general terms, in this thesis, as being the product of three operators:

$$T \equiv \epsilon U Z, \tag{3.40}$$

where Z is the operation of complex conjugation, U is a unitary transformation which reverses all spin projection (in $SO(3)$ this is the $2jm$ matrix just discussed) and ϵ is a conventional phase — dependent on the basis choice involved.⁵ In $SO(3)$ then, time-reversal could very well be the transformation that connects the two operations C and $O(\varphi)$, although all that is really needed

⁵With the Condon and Shortley basis ϵ is the parity operator $P = (-1)^{\sum_i l_i}$ (where $\sum_i l_i$ is the sum of the orbital angular momenta). With the Fano and Racah definition of the basis functions $\epsilon = 1$.

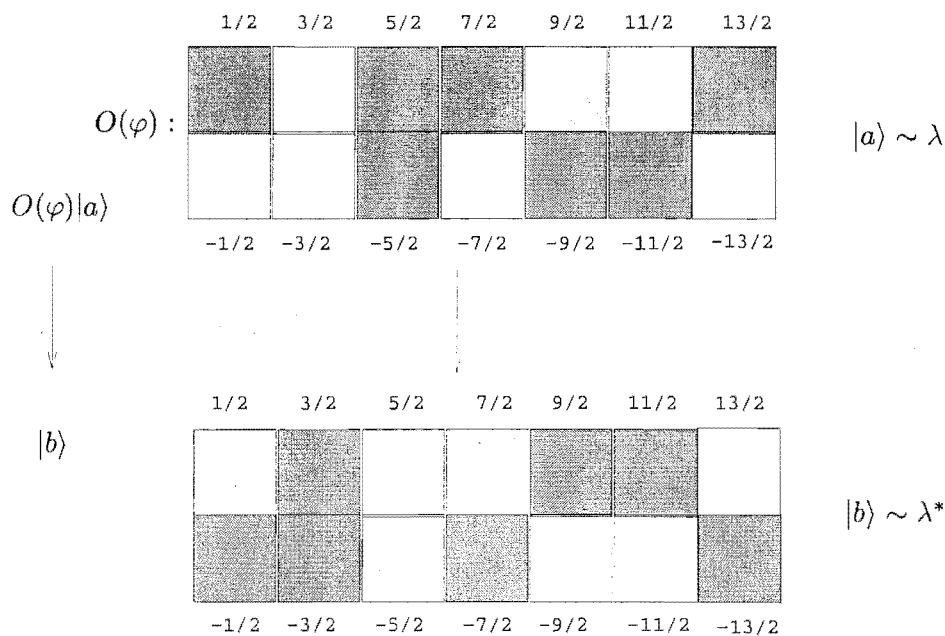


Figure 3.4: These two states do not transform similarly under rotations, but in fact as states complex conjugate to one another λ and λ^* . That is the action of $O(\varphi)$ takes the state $|a\rangle$ transforming as the irreducible representation λ , to the state $|b\rangle$ which transforms as λ^* . The operator $O(\varphi)$ has been defined in this way so as to ensure that the states $|a\rangle$ and $|b\rangle$ couple to an invariant (the closed shell). $O(\varphi)$ must be an antilinear operator — similar in nature to time-reversal T , see Figure 3.5.

is the $2j$ transformation $(-1)^{j-m}\delta_{m-m}$.

3.1.5 The relationship between C and HT

The definition of a time reversal operator T was given in general terms in § 3.1.4. In this subsection the effect of the operation of time reversal on second quantized operators is given explicitly. This enables the effect on second quantized expressions of the particle-hole conjugation operator to be compared with that of the combined operations of hermitian conjugation and time reversal. Also, at the close of this subsection, the phase choice inherent in Bell's [4] definition of C is made transparent and its implications discussed.

Given the definition of the time reversal operator, as stated in equation 3.1.4, T has the ef-

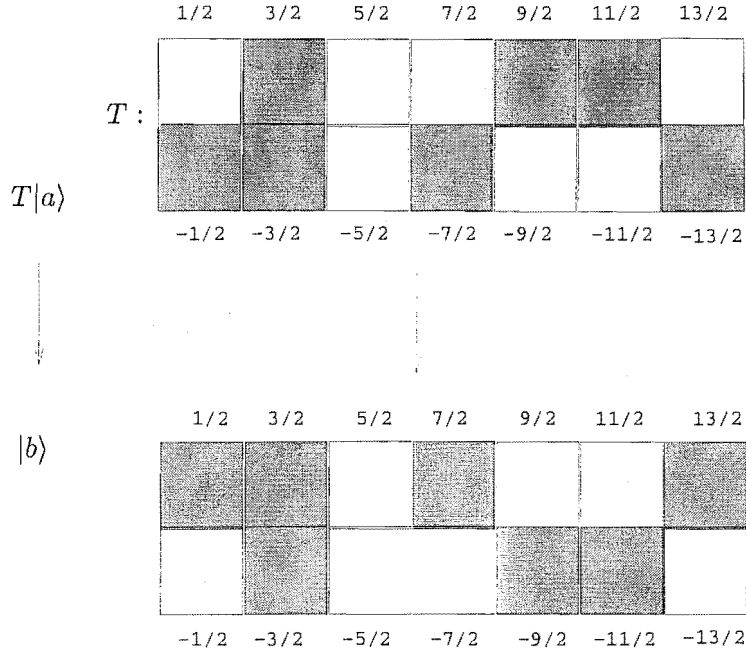


Figure 3.5: Time Reversal takes a state transforming as λ to one transforming as λ^* . It should be noted that for the irreducible representations of $SO(3)$, $\lambda^* \sim \lambda$. The situation for the point groups is slightly more complicated (see, for example, Lax [39] Chapter 10).

fect when acting on a creation operator a_{jm}^\dagger of

$$Ta_{jm}^\dagger T^{-1} = \epsilon(-1)^{j-m} a_{j-m}^\dagger. \quad (3.41)$$

A similar effect is had on the annihilation operator a_{jm} .

If the operation of hermitian conjugation (normally denoted by the dagger (\dagger) superscript) is instead expressed as the operator H (for algebraic convenience — and also to put all operators on an equal footing) then the action of H on a_{jm}^\dagger is given by

$$Ha_{jm}^\dagger H^{-1} = a_{jm}. \quad (3.42)$$

Combining these two operators T and H the effect is

$$(HT)a_{jm}^\dagger (HT)^{-1} = \epsilon(-1)^{j-m} a_{j-m}^\dagger. \quad (3.43)$$

In this regard T and H are seen to commute

$$(TH)a_j^\dagger(TH)^{-1} = \epsilon(-1)^{j-m}a_{j-m} \quad (3.44)$$

$$\text{i.e. } HT = TH. \quad (3.45)$$

In the definition of the time reversal operator T give in equation 3.1.4 a phase factor ϵ was included, prompting the question of why such a phase factor was not given by Bell [4] and what the implications of the inclusion of such a factor, if any, would be.

If the definition of C given in equation (3.13) is now made employing an indeterminate phase η then

$$Ca_{jm}^\dagger C^{-1} = \eta(-1)^{j-m}a_{j-m}. \quad (3.46)$$

That is, the action of C on one or more annihilation or creation operators is equivalent within a phase to the action of HT , (compare equations (3.43) and (3.46)). This could be considered a good reason for choosing this particular linear definition of C , i.e. based solely on their effects on lone annihilation/creation operators C is equivalent to the operator combination HT . It must be remembered, however, that C has quite a different effect upon the empty shell state $|0\rangle$ (c.f. equation 3.10),

$$C|0\rangle = \prod_{n=-j}^j a_{jn}^\dagger |0\rangle \equiv |c\rangle, \quad (3.47)$$

where $|c\rangle$ represents the filled shell and as emphasised in the discussion following the definition of C in § 3.1.2 care must be taken with the ordering of operators given in the product. From equation 3.10 the ordering of factors in the product is as follows:

$$\prod_{n=-j}^j a_{jn}^\dagger \equiv a_{jj}^\dagger a_{jj-1}^\dagger \cdots a_{j-j+1}^\dagger a_{j-j}^\dagger. \quad (3.48)$$

Hence

$$C^2|0\rangle = C|c\rangle \quad (3.49)$$

$$= \eta^{2j+1}(-1)^{j-j}a_{j-j}(-1)^{jj-j+1}a_{j-j+1}\dots(-1)^{jj+j-1}a_{jj-1}(-1)^{jj+j}a_{jj}C|0\rangle \quad (3.50)$$

$$= \eta^{2j+1}(-1)^{j(2j+1)}\left(\prod_{n=j}^{-j}a_{jn}\right)\left(\prod_{n=-j}^ja_{jn}^\dagger\right)|0\rangle \quad (3.51)$$

$$= \eta^{2j+1}(-1)^{j(2j+1)}|0\rangle. \quad (3.52)$$

Now the action of C^2 upon a partially filled state $|a\rangle$ of N particles is considered⁶:

$$C^2|a\rangle = C^2a_{jm}^\dagger a_{jn}^\dagger\dots|0\rangle \quad (3.53)$$

$$= \eta^{2N}(-1)^{2jN}\eta^{2j+1}(-1)^{j(2j+1)}|a\rangle \quad (3.54)$$

$$= \eta^{2j+1+2N}(-1)^{j(2j+1-2N)}|a\rangle. \quad (3.55)$$

This last relationship (equation (3.55)) and the action of C^2 on the filled shell $|c\rangle$ enables the phase η to be determined. From equation (3.52)

$$C^2|c\rangle = C(C^2|0\rangle) = \eta^{2j+1}(-1)^{j(2j+1)}|c\rangle. \quad (3.56)$$

From equation (3.55) with $|a\rangle$ now being the filled shell $|c\rangle$ (i.e. with $N = 2j + 1$)

$$C^2|c\rangle = \eta^{2j+1+2N}(-1)^{j(2j+1-2N)}|c\rangle \quad (3.57)$$

$$= \eta^{3(2j+1)}(-1)^{j(2j+1)}|c\rangle. \quad (3.58)$$

Comparing powers of η in equation (3.56) and (3.58) gives

$$\eta^{2(2j+1)} = 1. \quad (3.59)$$

From a similar consideration of the half-filled shell, $|a\rangle$, ($2N = 2j + 1$) it is found that

$$C^2|a\rangle = \eta^{2(2j+1)}|a\rangle. \quad (3.60)$$

⁶Where the relationship $(-1)^{2jN} = (-1)^{-2jN}$ holds as $2jN$ is an integral number

Reconciling equation (3.59) and (3.60) gives the result that

$$C^2|a\rangle = |a\rangle. \quad (3.61)$$

This is the same result as that which follows from equation (3.18), i.e. there is no loss in generality (at least as far as results for the half-filled shell are concerned) in Bell's choice of setting $\eta = 1$.

It is also entirely consistent with the Fano-Racah phase convention, i.e. setting $\epsilon = 1$ in

$$Ta_{jm}^\dagger T^{-1} = \epsilon(-1)^{j-m}a_{j-m}^\dagger, \quad (3.62)$$

and the previous statement, in the discussion following equation 3.46, that C is equivalent to HT when acting on lone annihilation/creation operators.

3.1.6 Selection rules for half-filled shell states

As has been shown in §3.1.3 half-filled shell states have the distinction of possessing a specific parity with respect to the particle-hole conjugation operator C , i.e. the eigenvalue of C^2 with respect to half-filled shells states is 1.

This leads to selection rules for half-filled shells which are similar in nature to the time reversal selection rules for states and operators of definite parity (see Stedman [58] and also §4.2.2.6, where the analogous behaviour of time reversal on angular momenta and particle-hole conjugation on quasispin is discussed).

These rules (or ones very similar) were first proposed by Ceulemans [12] in the situation of strongly coupled ligand fields. A statement of these rules is straightforward. If S is a single-particle, hermitian operator ($S^\dagger = S$) then

Selection Rules 3.1.1 *Half-filled shells*

1. *Off diagonal interaction elements between half-filled shell states of opposite parity with respect to C will be zero if S is anti-symmetric with respect to T (time odd).*

2. *Off diagonal interaction elements between half-filled shell states of identical parity with respect to C will be zero if S is symmetric under T (time even).*
3. *Diagonal interaction elements between half-filled shell states will be zero if S is symmetric under T and not totally symmetric under spatial symmetry operations (not scalar).*

For the proof of these statements let $|a\rangle$ and $|b\rangle$ denote half-filled shell states, i.e. eigenstates of C with eigenvalues ± 1 . For example

$$C|a\rangle = \pi_a|a\rangle, \quad (3.63)$$

where $\pi_a = +1$ (-1) if $|a\rangle$ has positive (negative) parity under C . Similarly for $|b\rangle$. The time reversed companions to $|a\rangle$ and $|b\rangle$ are denoted as $|\bar{a}\rangle$ and $|\bar{b}\rangle$. Either by the reasoning that if $|a\rangle$ and $|b\rangle$ are eigenstates of C so must be the time reversed states $|\bar{a}\rangle$ and $|\bar{b}\rangle$, or by the fact that C and T commute⁷ the following result is found

$$C|\bar{a}\rangle = \pi_a|\bar{a}\rangle, \quad \text{i.e.} \quad CT|a\rangle = \pi_a T|a\rangle. \quad (3.64)$$

In much the same manner as the derivation of equation (3.37), the matrix elements of

$$(\langle a| (CT)^{-1}) S ((CT)|b\rangle) \quad (3.65)$$

are found to be

$$(\langle a| (CT)^{-1}) S ((CT)|b\rangle) = \langle a|b\rangle \langle c| S|c\rangle - \langle a| S|b\rangle^*, \quad (3.66)$$

where $|c\rangle$ indicates the ket corresponding to the filled shell. For ease of notation let

$$B_{ab} \equiv (\langle a| (CT)^{-1}) S ((CT)|b\rangle), \quad (3.67)$$

$$S_{ab} \equiv \langle a| S|b\rangle \text{ and} \quad (3.68)$$

$$A \equiv \langle c| S|c\rangle. \quad (3.69)$$

Then equation (3.66) can be more easily written as

$$B_{ab} = \delta_{ab} A - S_{ab}^* \quad (3.70)$$

$$= \delta_{ab} A - S_{ba}. \quad (3.71)$$

⁷This is seen by considering the action of CT and of TC on an arbitrarily filled shell

In $SO(3)$ the reality of the coupling coefficients gives $S_{ab}^* \equiv S_{ab}$, but this relationship will not be exploited here in order to maintain the generality of the result. It will be shown in the next chapter that the same result (equation (3.71)) still holds in systems of reduced symmetry.

However (3.65) also provides

$$(\langle a | (CT)^{-1}) S ((CT) | b \rangle) = \pi_a \pi_b \langle a | \bar{S} | b \rangle^* \quad (3.72)$$

$$= pq \langle a | S | b \rangle^* \quad (3.73)$$

$$= pq S_{ba}, \quad (3.74)$$

where \bar{S} is shorthand for TST^{-1} , $q = +1$ (-1) if S is time even (odd) and $p = +1$ (-1) if $|a\rangle$ and $|b\rangle$ have identical (opposite) parity under C .

Equations (3.71) and (3.74) imply that

$$pq S_{ba} = A \delta_{ab} - S_{ab}, \quad (3.75)$$

from which the Selection Rules 3.1.1 follow⁸.

3.2 The LS-coupling scheme

3.2.1 Transition to the LS-coupling scheme

In this chapter the notation has so far been restricted to that pertaining to jj -coupling. This has simply been for convenience and clarity. It will now be shown that the transition can be made to the LS-coupling scheme in an entirely formal way.

The creation and annihilation operators in the LS-coupling scheme are written as

$$a_{lm_l sm_s}^\dagger, a_{lm_l sm_s} \quad (3.76)$$

⁸If S is not totally symmetric under spatial symmetry operations its expectation value A in the closed shell vanishes

and their anti-commutation relations are

$$\{a_{lm_lsm_s}^\dagger, a_{lm'_lm'_s}\} = \delta_{m_lm'_l} \delta_{m_sm'_s}, \quad (3.77)$$

all others being zero. The particle-hole conjugation operator now has the definition

$$C|0\rangle = \prod_{m_lm_s} a_{lm_lsm_s}^\dagger |0\rangle, \quad (3.78)$$

$$Ca_{lm_lsm_s}^\dagger C^{-1} = (-1)^{l+s-m_l-m_s} a_{l-m_l, s-m_s}. \quad (3.79)$$

The creation operators can now be considered to be double-tensor operators of rank l in orbital and rank s in spin space (in cases where LS-coupling is applicable spin and orbital angular momentum operators commute with each other and with the Hamiltonian. They are thus legitimate irreducible representation labels for the classification of states) and so are the annihilation operators into which they are transformed (as may be verified by checking their commutation relations with both the spin and orbital angular momentum operators — in second quantized form).

It follows that the operator C is therefore invariant under transformations in both the spin and orbital angular momentum spaces and hence conserves both quantum numbers. The equation below follows at once.

$$C^2 = (-1)^{(l+s)\{(2l+1)(2s+1)-2N\}} \quad (3.80)$$

where N is the particle number given by the operator

$$\hat{N} = \sum_{m_lm_s} a_{lm_lsm_s}^\dagger a_{lm_lsm_s}. \quad (3.81)$$

For half-filled shells $2N = (2l+1)(2s+1)$ and once again $C^2 = 1$.

The equation relating matrix elements of single-particle tensor operators of rank (k_l, k_s) follows from equation (3.37)

$$\langle b' | T_{q_l q_s}^{(k_l k_s)} | a' \rangle = \langle b | a \rangle \langle c | T_{q_l q_s}^{(k_l k_s)} | c \rangle - (-1)^{k_l+k_s} \langle b | T_{q_l q_s}^{\dagger(k_l k_s)} | a \rangle. \quad (3.82)$$

This is equivalent to equation (74) of Racah [43]⁹.

The matrix element of $T_{q_l q_s}^{(k_l k_s)}$ in the filled shell $|c\rangle$, must necessarily vanish if T is not scalar (completely symmetric under rotations) in both the spin and orbital angular momentum spaces. In this LS-coupling scheme of notation the Racah conjugate tensor is defined by

$$t_{m_l m_s n_l n_s}^{\dagger q_l q_s} = (-1)^{q_l + q_s} \{t_{n_l n_s m_l m_s}^{-q_l -q_s}\}^*. \quad (3.83)$$

The formal transition from the (jm) operators to the $(lm_l sm_s)$ operators is given by the linear combinations

$$a_{jm}^\dagger = \sum_{m_l m_s} \langle lm_l sm_s | lsjm \rangle a_{lm_l sm_s}^\dagger. \quad (3.84)$$

Hence the action of C on the a_{jm}^\dagger expressed in terms of the $a_{lm_l sm_s}^\dagger$ is

$$C a_{jm}^\dagger C^{-1} = \sum_{m_l m_s} \langle lm_l sm_s | lsjm \rangle (-1)^{l+s-m_l-m_s} a_{l-m_l s-m_s} \quad (3.85)$$

$$= \sum_{m_l m_s} \langle l-m_l s-m_s | lsjm \rangle (-1)^{l+s+m_l+m_s} a_{lm_l sm_s} \quad (3.86)$$

$$= \sum_{m_l m_s} (-1)^{l+s+j} \langle lm_l sm_s | lsj-m \rangle (-1)^{l+s+m_l+m_s} a_{lm_l sm_s} \quad (3.87)$$

$$= (-1)^{2(l+s)+j+m} \sum_{m_l m_s} \langle lm_l sm_s | lsj-m \rangle a_{lm_l sm_s} \quad (3.88)$$

$$= (-1)^{j-m} a_{j-m}. \quad (3.89)$$

It should be noted that this fixes the final equation in §3 of Bell [4] (in which the final expression has an erroneous dagger).

As Bell points out, the transformation due to C acting on the a_{jm}^\dagger is essentially that of C acting on the $j = l + s$ subshells simultaneously. The conclusion Condon & Shortley (Condon

⁹It should be noted that for a time odd, hermitian T , matrix elements vanish for self-conjugate states ($|a\rangle = C|a\rangle$) and where $k_l + k_s$ is even. This is a special case of more general selection rules which will be stated in §3.1.6.

& Shortley [16] Chapter 12) have made is that if some linear combination of states in the LS-coupling scheme is a state in the jj -coupling scheme, then the very same property holds for the same linear combination of particle-hole conjugate states. Thus the transformation between the two schemes can be taken to be the same for a group of particles as for the conjugate group of holes.

3.2.2 Seniority

The seniority number concept was first introduced by Racah in 1943 (Racah [44]) to aid in the classification of states of d^n and f^n . It enabled Racah to connect the configuration l^n with the corresponding configuration l^{n-2} and as such it is intimately related with the concept of coefficients of fractional parentage (cfp) which was also introduced¹⁰ by Racah to aid in the building up of states, one electron at a time.

Expressed in the language and terms already in use in this chapter, the seniority number ν is the number of states in the configuration which are not “zero-coupled” (see §3.1.3). It is clear that an entire chain of states $\dots, l^{n-4}, l^{n-2}, l^n$ may be constructed by the addition of two zero-coupled states to the previous configuration in the chain. The configurations in the chain thus constructed can be seen to possess the same seniority number ν . Again the diagrammatic mnemonic from §3.1.3 proves useful in visualizing this process. As can be seen from Figure 3.6, the initial and final configurations, $|i\rangle$ and $|f\rangle$, in the chain are particle-hole conjugates of one another

$$|f\rangle = C|i\rangle. \quad (3.90)$$

One obvious but important implication of this is that particle-hole conjugate states have the same seniority. This fact enables a connection to be made between the second of the Selection Rules 3.1.1 and theorem 3.12-1 of Watanabe [61] which states that:

Matrix elements of a single electron even operator are zero

¹⁰Racah adapted the concept from Goudsmit and Bacher, Racah's coefficients were n times the square of theirs, and are the form commonly used today

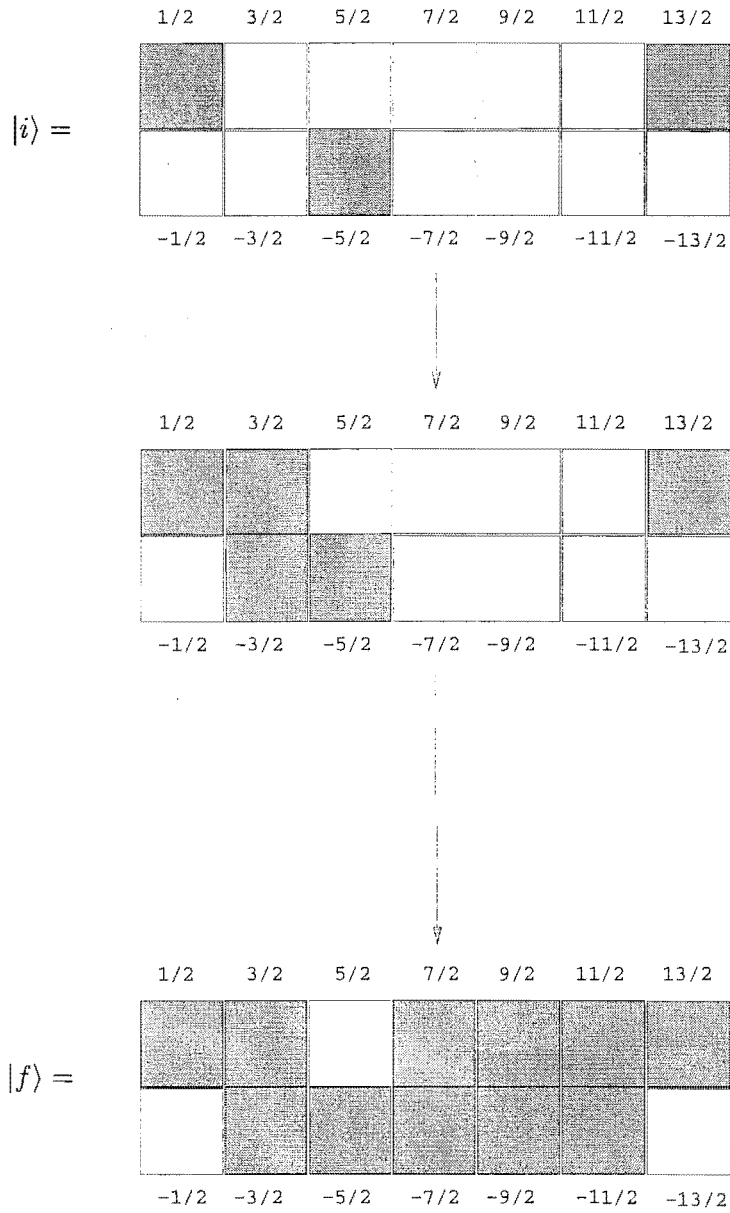


Figure 3.6: Diagrammatic representation of the building up process of a chain of states, each with the same seniority number ($\nu = 3$), via the iterative addition of a pair of zero coupled states. It should be noted that the number of empty states (holes) in $|f\rangle$, the final configuration, is equal to the number of occupied states in $|i\rangle$, the initial configuration. In fact the initial and final states are connected by the particle-hole conjugation operator C , i.e. $|f\rangle = C|i\rangle$.

when they are diagonal in the seniority.

The second rule in Selection Rules 3.1.1 can be seen to be consistent with Watanabe's by considering a special case of this where the matrix elements in question are taken between half-filled shell states which are particle-hole conjugates of one another. Obviously these states will have the same C parity as each other and, as discussed above, will also have the same seniority number. Criteria for both the second of Selection Rules 3.1.1 and for Watanabe's 3.12-1 are met if the single-particle operator is time even.

3.2.3 Quasispin

As its name suggests, the concept of quasispin refers to a set of operators which undergo commutation relations very similar in nature and form to those corresponding to the angular momentum operators (spin and orbital). The commutation relations for angular momentum operators in cartesian components are:

$$[\hat{s}_i, \hat{s}_j] = \epsilon_{ijk} \hat{s}_k, \quad i, j, k = x, y, z. \quad (3.91)$$

With normalized spherical co-ordinates

$$\hat{s}_+ = \frac{1}{\sqrt{2}}(\hat{s}_x + i\hat{s}_y), \quad (3.92)$$

$$\hat{s}_- = \frac{1}{\sqrt{2}}(\hat{s}_x - i\hat{s}_y) \quad \text{and} \quad (3.93)$$

$$\hat{s}_0 = \hat{s}_z, \quad (3.94)$$

these commutation relations may be expressed as

$$[\hat{s}_0, \hat{s}_+] = +\hat{s}_+, \quad (3.95)$$

$$[\hat{s}_0, \hat{s}_-] = -\hat{s}_- \quad \text{and} \quad (3.96)$$

$$[\hat{s}_+, \hat{s}_-] = \hat{s}_0. \quad (3.97)$$

The operators \hat{s}_+ and \hat{s}_- are ladder operators, \hat{s}_+ creates and \hat{s}_- destroys, quanta of angular momentum.

The ladder operators of quasispin will also be defined in such a way as to create or destroy

quanta of angular momentum, but in a very special way. Initially these definitions will be given for just one spin orbital, with the understanding that the extension of the definition to incorporate the entire shell is provided by summing over all the orbitals $m_l = -l$ to l .

The creation operator of quasispin, \hat{Q}_+ , will be defined to create a pair of zero-coupled (or as Watanabe describes them “Kramer’s Conjugate”) states — a pair of states with all components of angular momenta (possibly spin, orbital, total, or even iso-spin in Bell’s [4] case) are coupled to zero.

In a similar manner the quasispin annihilation operator is defined in such a way so as to destroy such zero-coupled states.

The second quantized operators

$$\hat{Q}_+ = \frac{1}{2}[s]^{\frac{1}{2}}[l]^{\frac{1}{2}}(\underline{a}^\dagger \underline{a}^\dagger)^{(00)} \quad (3.98)$$

$$\hat{Q}_- = -\frac{1}{2}[s]^{\frac{1}{2}}[l]^{\frac{1}{2}}(\underline{a} \underline{a})^{(00)} \quad (3.99)$$

$$\hat{Q}_0 = -\frac{1}{4}[s]^{\frac{1}{2}}[l]^{\frac{1}{2}}\{(\underline{a}^\dagger \underline{a})^{(00)} + (\underline{a} \underline{a}^\dagger)^{(00)}\} \quad (3.100)$$

as given by Judd (see, for example, Judd [29] or Judd [32]) meet the specified criteria.

The notation of Judd’s perhaps requires explanation. It was mentioned in §3.1.2 that the operator $(-1)^{l+s-m_l-m_s} a_{l-m_l s-m_s}$ “transforms in the same way” as $a_{lm_l sm_s}^\dagger$ and that both are components of double tensors of rank l in the orbital space and rank s ($= \frac{1}{2}$) in the spin space. \underline{a}^\dagger refers to the tensor whose components are $a_{lm_l sm_s}^\dagger$ and \underline{a} refers to the tensor whose components are $(-1)^{l+s-m_l-m_s} a_{l-m_l s-m_s}$. The \underline{a}^\dagger and \underline{a} may be coupled like any other tensors, thus $(\underline{a}^\dagger \underline{a})^{(\kappa k)}$ for instance indicates a coupling of the spin spaces to κ and to orbital spaces to k . That is

$$(\underline{a}^\dagger \underline{a})^{(\kappa k)} = \sum_{m_l m'_l m_s m'_s} (-1)^{l+s-m_l-m_s} \langle lm_l l' m'_l | kq \rangle \langle sm_s s' m'_s | \kappa p \rangle a_{lm_l sm_s}^\dagger a_{l-m_l s-m_s}. \quad (3.101)$$

In addition, the use of $[x]$ is simply a shorthand for $(2x+1)$.

That the components of the quasispin vector \underline{Q} satisfy the familiar commutation relations for the components of an angular momentum vector may be verified by the expansion of the tensor couplings in equations (3.98)–(3.100), as may the statement that the components of quasispin commute with those of the spin and orbital angular momentum vectors (which is apparent as quasispin was constructed to be scalar in these two quantities).

The ladder operators \hat{Q}_+ and \hat{Q}_- were constructed to add or delete pairs of electrons coupled to a 1S state (“zero-coupled”, or “Kramer’s Conjugate” pairs), connecting states of a shell which have the same seniority number. And it can be seen from its definition that \hat{Q}_0 is a variant of the number operator. The eigenvalue of \hat{Q}_0 is simply Q , and its projection is

$$M_Q = -\frac{1}{2}(2l + 1 - N). \quad (3.102)$$

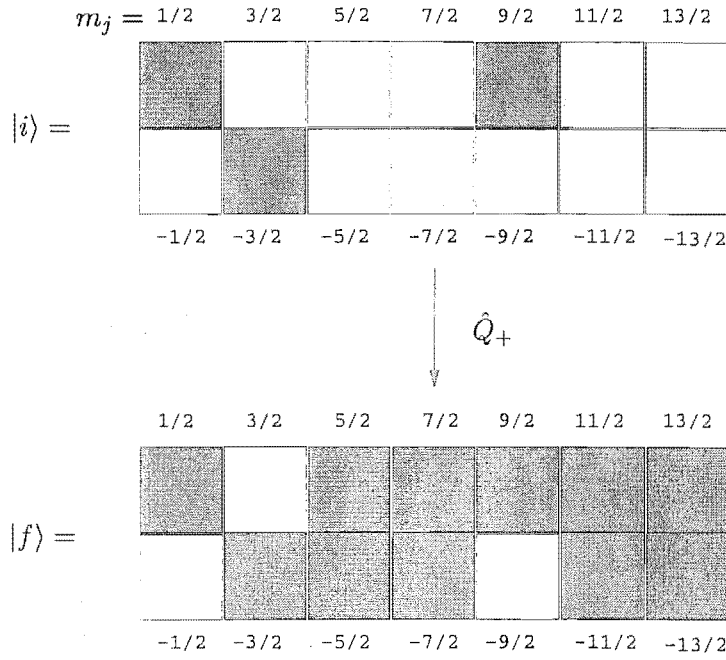
It can be shown (for example see Stedman [56]) that the eigenvalue of \hat{Q}_0 acting on one column of a diagram such as in Figure 3.7, gives $-\frac{1}{2}$ if both cells in the column are filled $+\frac{1}{2}$ if both are empty and 0 if only one of the upper or lower cells is occupied. Quasispin for the entire shell is the sum of these.

As hinted previously there exists an intimate relationship between Q , ν and the occupancy number of the shell, N . Yet again the diagram mnemonic proves useful. Figure 3.7 depicts a state $|i\rangle$ with $N = \nu = 3$ and $Q = 2$. If this state is acted upon repeatedly by the shift operator \hat{Q}_+ the maximum number of times possible, state $|f\rangle$ is produced with $\nu = 3$, $N = 2(2l + 1) - \nu = 11$ and $Q = \frac{1}{2} \times (\text{Number of filled columns}) = \frac{1}{2}((2l + 1) - \nu)$.

Since Q is unchanged by addition or deletion of zero coupled states it is seen that in all cases the relationship between quasispin Q and seniority ν is

$$Q = \frac{1}{2}(2l + 1 - \nu). \quad (3.103)$$

In the instance of the half-filled shell $N = 2l + 1$ it is seen that $M_Q = 0$. For less (greater) than half-filled shells M_Q is positive (negative).

Figure 3.7: The action of \hat{Q}_+ on a partially filled shell.

3.2.3.1 Triple Tensor Notation

It has already been discussed how the vector \underline{Q} commutes with both \underline{S} and \underline{L} . This enables the construction of a so called triple tensor operator. The two double tensors \underline{a}^\dagger and \underline{a} may be considered to be the components of the triple tensor $\underline{a}^{(qsl)}$ for which the projection of q is $m_q = +\frac{1}{2}$ and $-\frac{1}{2}$ respectively. From equation (3.102) it is straightforward to see that the particle-hole exchange given by $N \rightarrow 2(2l+1) - N$ reverses the sign of M_Q . Thus as Judd [29, 32] and Stedman [56] point out, particle-hole conjugation C is to \underline{Q} what time reversal is to \underline{S} or \underline{L} .

Judd also points out that the fact that both s and q are $\frac{1}{2}$ provides the symmetry of exchange between spin and quasispin spaces, which may be exploited.

3.2.4 Commutation relations of C and \underline{Q}

It has previously been mentioned (§3.1.3) that there exists two equally valid choices for the particle-hole conjugation operator C with respect to linearity¹¹. Both choices have their merits, but choosing C to be antiunitary (i.e. antilinear and unitary) provides some rather nice results with regard to quasispin.

If the operation of complex conjugation, Z , is added to the definition of C given in equation (3.13), then upon expansion of the equations defining quasispin (equations (3.98)–(3.100)) into their cartesian components it is found that this new antilinear C , denoted by C_A , anti-commutes with every Cartesian component of \underline{Q} . That is

$$\{C_A, \underline{Q}\} = 0. \quad (3.104)$$

In this the operation of complex conjugation is vital, for without it, the operation of the linear C , now denoted C_L , invokes a rotation in \underline{Q} space, i.e.

$$C_L Q_x C_L^{-1} = -Q_x \quad (3.105)$$

$$C_L Q_y C_L^{-1} = Q_y \quad (3.106)$$

$$C_L Q_z C_L^{-1} = -Q_z. \quad (3.107)$$

Of the various authors using particle-hole conjugation in this operator form, Judd [29], Stedman [56] and Ceulemans [12] all use some variant of the antilinear C (C_A). Bell and Keiter et al. [34], however, use a linear C , (C_L).

¹¹It is clear that all equivalent choices for an antilinear C must be equivalent to within an unitary transformation. See, for example, the antilinear choices for the particle-hole conjugation operator made by Stedman (§4.2) and Ceulemans (§4.3). Similarly for all choices of C being linear.

Chapter 4

Quasispin in fields of reduced symmetry

This chapter consists of three sections, corresponding to the works of three giants in the field of quasispin and particle-hole conjugation in cases of reduced symmetry — Wybourne (see Wybourne [65] and Wybourne [67]), Stedman [56] and Ceulemans (see Ceulemans [12] and Ceulemans [13]). All three of these authors take a highly unique approach to the common problem of defining quasispin and particle-hole conjugation operators in instances where the symmetry is not $SO(3)$.

In §4.1 Wybourne’s 1973 paper “Lie Algebras in Quantum Chemistry: Symmetrized Orbitals” [65] is examined. It will be seen that Wybourne takes the highly unusual step of using the methods of inner plethysms to ascertain how to and when it is possible to embed a finite group in a Lie group chain. After discussing Wybourne’s example of quasispin classification of terms for an icosahedral splitting symmetry, an original example for the case of octahedral symmetry is worked through. It is noted here that these results are identical to those obtained by Ceulemans [13] in 1994 by more conventional methods.

§4.2 uses as its basis Stedman’s paper of 1987 (Stedman [56]), who took the original approach of generalising Judd’s [29] technique of viewing the second quantized annihilation and creation

operators as irreducible tensor operators, and quasispin operators as a very special instance of coupling these operators together.

Stedman's attempt to also generalize Judd's antiunitary particle-hole conjugation operator and the inconsistencies inherent in Stedman's approach are discussed in §4.2.2.6. The "corrected" generalized operators of quasispin and particle-hole conjugation are then developed and discussed. For this the techniques of "housekeeping" (checking for biparticity) as outlined in Chapter 2 are used heavily.

The effect the newly developed, antiunitary, particle-hole conjugation operator has on the cartesian components of quasispin is also discussed in §4.2.2.6. It will be seen there that "particle-hole conjugation is to quasispin as time reversal is to spin". It is also stated that this new operator is equivalent to one developed by Ceulemans [12] in 1984. How this is so is left to §4.3 to discuss.

§4.3 is devoted to a discussion of not just one, but two of Ceulemans' papers. In 1984 Ceulemans published an article (see Ceulemans [12]) in a Belgian journal in which he used the method of a Laplacian expansion of an electronic state represented in terms of a Slater determinant. This article proved to be the inspiration for this thesis, for at its conclusion Ceulemans outlined a set of selection rules with the quite remarkable implication that all linear Jahn-Teller activity is forbidden for half-filled ligand shells.

In §4.3.4 the identification of Ceulemans' antilinear particle-hole conjugation operator $O(\varphi)$ as being equivalent to the operator C'_A developed in §4.2.2.6, is made. Ceulemans' selection rules are rederived using the properties of C'_A and after the effects of C'_A and various other operators on single-particle unit-tensor operators are ascertained. Thus the results of Ceulemans' 1984 paper are obtained in such a way as to be more acceptable by most physicists.

§4.3.9 investigates the remarkable fact that Ceulemans in a 1994 article (see Ceulemans [13]) managed to rederive his own selection rules of 1984 by yet another (third) method, based on

results given by Wybourne in 1991 (see Wybourne [67]), and yet was unable to resolve the two formalisms. This is achieved in §4.3.10, and the connection between all three methodologies is made transparent. In addition, the selection rules for half-filled shells are shown to be equivalent to a statement about the parity of the states and the interaction operator with respect to (linear) particle-hole conjugation.

Throughout this chapter the concept of time reversal in fields of reduced symmetry is used extensively. It is assumed that the reader is somewhat familiar with this concept already as no attempt has been made to summarize this topic in this thesis. The reader is referred to Stedman and Butler [58] for an indepth and cohesive discussion of this vital subject.

4.1 Quasispin and Lie group chains

In 1973 Wybourne published a landmark paper “Lie Algebras in Quantum Chemistry: Symmetrized Orbitals” [65], which constructed a supergroup and its subgroups in such a way as to include the quasispin group $SU^Q(2)$, all by using the properties of second-quantized annihilation and creation operators. While the paper borrowed heavily from the earlier review article of Judd [30] it was original in that Wybourne’s operators carried the irreducible representation labels of finite groups and, for the first time, showed how to properly embed finite groups into such a group chain.

Wybourne outlines the procedure for applying Lie algebras to symmetry problems in quantum chemistry in a series of steps:

1. Construct the supergroup of the problem at hand and determine its relevant subgroup structures.
2. Classify the states of the system using preferably the quasispin scheme (explicit basis state construction not required).
3. Compute the relevant coupling coefficients.

4. Use the coupling coefficients to expand the interactions out in terms of operators having well defined transformations properties with respect to the same group scheme used to classify the states.
5. Apply the Wigner-Eckart theorem to compute the necessary matrix elements.

According to Wybourne during 1973 the first two steps were essentially complete and the third well advanced. The remaining steps only really required the results of the third. As this vital third step in the intervening time has been virtually completed for all the groups of interest and the methods of calculation of such coefficients covered in detail elsewhere (see Wybourne [64]) this section will give a brief synopsis of the remaining steps as detailed in Wybourne [65].

4.1.1 Irreducible representation labelling of the second-quantized operators

In a similar manner to the case of atomic theory where the set of quantum numbers $\xi = nslm_s m_l$ label the annihilation and creation operators, a_ξ and a_ξ^\dagger respectively, which satisfy the anticommutation relations

$$\{a_\xi^\dagger, a_\eta^\dagger\} = \{a_\xi, a_\eta\} = 0 \quad \text{and} \quad \{a_\xi^\dagger, a_\eta\} = \delta_{\eta\xi}, \quad (4.1)$$

the second quantized operators corresponding to states of an electron moving in a symmetry field characterized by some finite group G are distinguished by the labels

$$\xi = \Gamma_{a\alpha}, m_s, \quad (4.2)$$

where $\Gamma_{a\alpha}$ is the α th component of the λ dimensional irreducible representation Γ_a of G and m_s labels the two components of the basic spinor representation σ of $SU^S(2)$ (see, for example, Griffith [23] Chapter 9).

The 2λ creation operators a_ξ^\dagger are generators of the direct product group¹ $SU^S(2) \times G$.

The total number of possible states, as occupation number n goes from 0 to 2λ is calculated as

¹The "S" superscript on the group specifier $SU(2)$ should be noted. This is to distinguish the spin irreducible representations from, for example, those of quasispin which will be discussed in §4.1.3.

follows:

For each n there exists $\binom{2\lambda}{n}$ possible states so the total possible is given by

$$\sum_{n=0}^{2\lambda} \binom{2\lambda}{n}. \quad (4.3)$$

This summation may be calculated by² using a property of the function $\binom{2\lambda}{n} \equiv \frac{(2\lambda)!}{(2\lambda-n)!n!}$,

$$\binom{2\lambda}{n} = \binom{2\lambda-1}{n-1} + \binom{2\lambda-1}{n} \quad (4.4)$$

to give via induction

$$\sum_{n=0}^{2\lambda} \binom{2\lambda}{n} = 2^{2\lambda}. \quad (4.5)$$

Hence the particular irreducible representation of interest in the supergroup must be of degree $2^{2\lambda}$.

4.1.2 Formation of the supergroup and algebra

A Lie algebra is formed by constructing a set of operators closed under commutation. The set of $2 \times 2\lambda$ operators a_ξ^\dagger, a_ξ is *not* such a set. However if the $2 \times \binom{2\lambda}{2}$ operators $a_\gamma^\dagger a_\varepsilon^\dagger, a_\gamma a_\varepsilon$ ($\gamma \neq \varepsilon$) are taken along with the $(2\lambda)^2$ operators $a_\gamma^\dagger a_\varepsilon$ and the $2 \times 2\lambda$ operators a_ξ^\dagger, a_ξ , the complete set of $2\lambda(4\lambda + 1)$ operators obtained is closed under commutation.

If now the subset of 2λ operators

$$H_\xi = \frac{1}{2}[a_\xi^\dagger, a_\xi] \quad (4.6)$$

is considered it is seen that they form a set of self commuting operators (an example of “Weyl self commuting” operators).

²This result may also be verified by adding the entries in the 2λ th row of Pascal’s triangle

It is seen that the commutation relations of the H_ξ with every element of the $2\lambda(4\lambda + 1)$ set of $E_{\alpha\epsilon}$, a_η^\dagger , a_η , $a_\eta^\dagger a_\zeta^\dagger$, $a_\eta a_\zeta$, $a_\eta^\dagger a_\zeta$ returns that same set. In fact

$$[H_\xi, E_\alpha] = \alpha_\xi E_\alpha. \quad (4.7)$$

Explicitly

$$[H_\xi, a_\eta^\dagger] = \delta_{\xi\eta} a_\eta^\dagger \quad (4.8)$$

$$[H_\xi, a_\eta] = -\delta_{\xi\eta} a_\eta \quad (4.9)$$

$$[H_\xi, a_\eta^\dagger a_\zeta^\dagger] = (\delta_{\xi\eta} + \delta_{\xi\zeta}) a_\eta^\dagger a_\zeta^\dagger \quad (4.10)$$

$$[H_\xi, a_\eta a_\zeta] = -(\delta_{\xi\eta} + \delta_{\xi\zeta}) a_\eta a_\zeta \quad (4.11)$$

$$[H_\xi, a_\eta^\dagger a_\zeta] = (\delta_{\xi\eta} - \delta_{\xi\zeta}) a_\eta^\dagger a_\zeta. \quad (4.12)$$

It is said that the E_α are eigenvectors of the H_ξ . The roots α , of which the α_ξ are components, can be represented in terms of 2λ mutually orthogonal unit vectors \underline{e}_i ($i = 1, 2, \dots, 2\lambda$) to give the $2\lambda(4\lambda + 1)$ roots $\pm \underline{e}_i$, $\pm \underline{e}_i \pm \underline{e}_j$ (see, for example, Wybourne [66] Chapter 6). For example with $\lambda = 1$ the roots may be plotted on a two dimensional weight diagram (see Figure 4.1) which, as

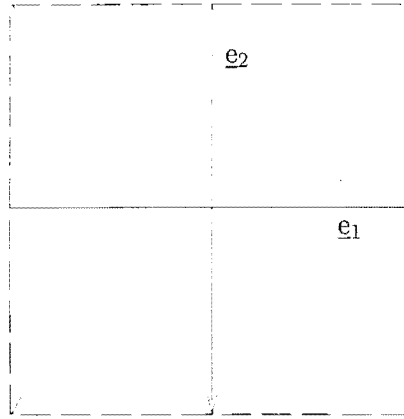


Figure 4.1: The two dimensional weight diagram for $\lambda = 1$. This corresponds to Cartan's Lie algebra B_2 .

may be verified, corresponds to Cartan's Lie algebra B_2 . These 10 root vectors (including 2 null root vectors) may be associated with the $SO(5)$ Lie algebra.

In general the 2λ root vectors, giving the $2\lambda(4\lambda + 1)$ roots \underline{e}_i , $\pm \underline{e}_i \pm \underline{e}_j$ correspond to the root

scheme of the Lie algebra denoted by Cartan as $B_{2\lambda}$ and associated with the special orthogonal group in $4\lambda + 1$ dimensions $SO(4\lambda + 1)$.

By considering the action of H_ξ on an arbitrary n -particle determinantal state

$$H_\xi(\alpha, \beta, \dots, \omega) = (a_\xi^\dagger a_\xi - \frac{1}{2}) a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger |0\rangle \quad (4.13)$$

it can be seen that the 2λ H_ξ operators generate weight vectors (Judd [30]) all of the form $[\pm\frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2} \dots \pm \frac{1}{2}]$, because $(a_\xi^\dagger a_\xi - \frac{1}{2})$ gives $\frac{+1}{2}$ if the state ξ is occupied, $\frac{-1}{2}$ if not.

Each determinantal state is associated with a unique weight vector. The highest weight is $[\frac{1}{2} \frac{1}{2} \frac{1}{2} \dots \frac{1}{2}]$, hence the complete set of $2^{2\lambda}$ states must span the single $2^{2\lambda}$ degree irreducible representation $[\frac{1}{2} \frac{1}{2} \frac{1}{2} \dots \frac{1}{2}]$ of the group $SO(4\lambda + 1)$. Therefore $SO(4\lambda + 1)$ is the supergroup desired.

Wybourne then goes on to examine the subgroup structure of this supergroup. As he points out, subgroups are not hard to find. The general procedure is to discard one or more subsets of the operators $a_\eta^\dagger, a_\eta, a_\eta^\dagger a_\zeta^\dagger, a_{\eta\zeta}, a_\eta^\dagger a_\zeta^\dagger$ in such a way that the remaining operators still form a group. In the same way that the supergroup $SO(4\lambda + 1)$ was shown to correspond to Cartan's Lie Group designation $B_{2\lambda}$, root-vector diagrams may be found for these subgroups, and by comparing diagrams with those in, for example, Racah [46] the correspondence discovered.

4.1.3 The quasispin group

A subgroup of particular interest is that of quasispin. According to Wybourne, Sviridov & Smirnov [59] were the first to introduce quasispin into strong crystal fields — although not with an overlying group scheme.

Wybourne defines the three generators of the quasispin group $SU^Q(2)$,

$$Q_+ = \frac{1}{2} \sum_{\xi} (-1)^{s-m_s} a_{\xi}^{\dagger} a_{\xi'}^{\dagger} \quad (4.14)$$

$$Q_- = \frac{1}{2} \sum_{\xi} (-1)^{s-m_s} a_{\xi} a_{\xi'} \quad (4.15)$$

$$Q_0 = \frac{1}{2} \left(\sum_{\xi} a_{\xi}^{\dagger} a_{\xi} - \lambda \right), \quad (4.16)$$

where $\xi = \Gamma_{a\alpha}, m_s$ and $\xi' = \Gamma_{a\alpha'}, -m_s$. The group is called $SU^Q(2)$ since the commutation relations of the generators are identical to those of the spin operators which generate $SU^S(2)$.

For example

$$[Q_0, Q_+] = Q_+ \quad (4.17)$$

$$[Q_0, Q_-] = -Q_- \quad (4.18)$$

$$[Q_+, Q_-] = 2Q_0. \quad (4.19)$$

These may be checked by expansion using equations (4.1). The operator $\sum_{\xi} a_{\xi}^{\dagger} a_{\xi}$ is readily recognised as being the number operator counting the number of occupied states in the shell, and hence the eigenvalues M_Q of Q_0 are simply

$$M_Q = (n - \lambda)/2. \quad (4.20)$$

By inspection it can be seen that the operators Q_+ and Q_- raise or lower, respectively, n by 2.

All this is highly analogous to the situation in $SO(3)$ (see §3.2.3). It is found that the generators of quasispin commute with those of both the symplectic $Sp(2\lambda)$ — and the unitary symplectic $USp(2\lambda)$ — groups, and Wybourne establishes the group-subgroup chain³

$$\begin{aligned} U(2^{2\lambda}) \supset SO(4\lambda + 1) \supset SO(4\lambda) \supset SU^Q(2) \\ \times (USp(2\lambda) \supset SU^S(2) \times (O(\lambda) \supset SO(\lambda))) . \end{aligned} \quad (4.21)$$

Since the irreducible representations of the symplectic group are $\langle 1^{\nu} \rangle$, where $\nu = n, n-2, n-4$

³It is important to note that while $SU^S(2) \times O(\lambda)$ is a subgroup of $USp(2\lambda)$ ($=U(1) \times Sp(2\lambda)$) it is not a subgroup of $Sp(2\lambda)$, (although $SU^S(2) \times SO(\lambda)$ is)

is the seniority number discussed in §3.2.2, the above result implies that the actions of Q_{\pm} are limited to states of fixed seniority. The maximal eigenvalue of Q_0 occurs when $\nu = n$. Hence states of a given ν transform under $SU^Q(2)$ as states of quasispin.

Analogously to the spin and orbital angular momentum cases, where the maximum values of $|M_S|$ and $|M_L|$ are written as S and L , the maximum value of $|M_Q|$ is simply

$$Q = \frac{1}{2}(\nu - \lambda). \quad (4.22)$$

This is as far as it is possible to go, as far as chains of continuous groups are concerned. The only way forward from here is through the embedding of finite groups in the group chain.

It is only necessary, however, to consider the embedding of the symmetric (S_n) and alternating (A_n) groups since Cayley's theorem (see, for example, Wybourne [64] §2.5) states that "every group G of order n is isomorphic with a subgroup of S_n ".

4.1.4 Embedding of finite groups in Lie group chains

Butler & King [10] and King [36] considered the very non-trivial general problem of embedding S_n and A_n in various Lie groups. It is found that there are certain restrictions on this embedding procedure. The dimension of the irreducible representation of the symmetric group μ , i.e. $f^{(\mu)}$, must equal N , where N is the order of the group $SO(N)$. This means the irreducible representation μ must be faithful and unimodular (see King for more details). Fortunately (4.21) is one of three group chains and at least one chain is always appropriate.

Branching rules for the nested Lie groups appearing in the group chain may either be calculated manually from the method of outer plethysms of S -functions or read from tables, both of which are to be found in Wybourne's book [64].

Similarly the branching rules for going from a compact Lie group to a finite group isomorphic to either a symmetric or alternating group may be found by the inner plethysm of S -functions

(see Butler and King).

A table correlating certain finite groups with the appropriate symmetric and alternating groups is to be found in Table 4.1. In this manner it is possible to determine all the relevant branching

$D_3 \sim S_3$	$O \sim T_d \sim S_4$	$T \sim A_4$	$I \sim A_5$
$A_1(3)$	$A_1(4)$	$A_1 \{4\}$	$A \{5\}$
$E(21)$	$T_2(31)$	$T \{31\}$	$U \{41\}$
$A_2(1^3)$	$E(2^2)$	$E \left\{ \begin{array}{l} \{21\} + \\ \{21\} - \end{array} \right.$	$V \{32\}$
	$T_1(21^2)$		$T_1 \{31^2\} +$
	$A_2(1^4)$		$T_2 \{31^2\} -$

Table 4.1: Correlations with S_m and A_m representations. The numbers in parentheses indicate irreducible representations of the symmetric group, whilst numbers between barred parentheses ($\{ \}$) indicate irreducible representations of the alternating group. This table is an adaptation of Table 2 in Wybourne [65].

rules without having to refer to tables of finite group characters.

Wybourne gives an example for icosahedral $\sim A_5$ symmetry. For instance, the terms associated with t_1 or t_2 orbitals (both of dimension $\lambda = 3$) can be found by considering the $SO(3) \rightarrow A_5$ mappings

$$[1] \rightarrow t_1 \quad (4.23)$$

$$\text{and } [1] \rightarrow t_2. \quad (4.24)$$

The results of which are given in Tables 4.2 and 4.3 for t_1^n and t_2^n (where $n = 0$ to 6) respectively.

It is found in both cases that the states are completely designated by the group labels

$$|QM_Q SM_S \Gamma_{\alpha\alpha}\rangle. \quad (4.25)$$

It should be noted that the labels Q and M_Q carry exactly the same information as ν and n .

SO(13)	SO(12)	$SU^Q(2) \times Sp(6)$	$SU^S(2) \times SO(3)$	$SU^S(2) \times I$
$[\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}]$	$\left\{ \begin{array}{l} [\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}] \\ \\ \\ [\frac{1}{2} \frac{1}{2} \dots -\frac{1}{2}] \end{array} \right\}$	$\left\{ \begin{array}{l} 4\langle 0 \rangle \\ \\ 2\langle 1^2 \rangle \end{array} \right\}$	$\left\{ \begin{array}{l} 1[0] = 1S \\ 3[1] = 3P \\ 1[2] = 1D \end{array} \right\}$	$\begin{array}{l} 1A \\ 3T_1 \\ 1V \end{array}$
		$\left\{ \begin{array}{l} 3\langle 1 \rangle \\ \\ 1\langle 1^3 \rangle \end{array} \right\}$	$\left\{ \begin{array}{l} 2[1] = 2P \\ 4[0] = 4S \\ 2[2] = 2D \end{array} \right\}$	$\begin{array}{l} 2T_1 \\ 4A \\ 2V \end{array}$

Table 4.2: Icosahedral Symmetry: terms for n electrons in the t_1 orbital in the quasispin scheme. This is an adaptation of Table 8 in Wybourne [65]. Left superscripts denote either $2Q + 1$ or $2S + 1$, where appropriate.

SO(13)	SO(12)	$SU^Q(2) \times Sp(6)$	$SU^S(2) \times SO(3)$	$SU^S(2) \times I$
$[\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}]$	$\left\{ \begin{array}{l} [\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}] \\ \\ \\ [\frac{1}{2} \frac{1}{2} \dots -\frac{1}{2}] \end{array} \right\}$	$\left\{ \begin{array}{l} 4\langle 0 \rangle \\ \\ 2\langle 1^2 \rangle \end{array} \right\}$	$\left\{ \begin{array}{l} 1[0] = 1S \\ 3[1] = 3P \\ 1[2] = 1D \end{array} \right\}$	$\begin{array}{l} 1A \\ 3T_2 \\ 1V \end{array}$
		$\left\{ \begin{array}{l} 3\langle 1 \rangle \\ \\ 1\langle 1^3 \rangle \end{array} \right\}$	$\left\{ \begin{array}{l} 2[1] = 2P \\ 4[0] = 4S \\ 2[2] = 2D \end{array} \right\}$	$\begin{array}{l} 2T_2 \\ 4A \\ 2V \end{array}$

Table 4.3: Icosahedral Symmetry: terms for n electrons in the t_2 orbital in the quasispin scheme. This is an adaptation of Table 9 in Wybourne [65]. Left superscripts denote either $2Q + 1$ or $2S + 1$, where appropriate.

Terms for the five-fold degenerate v^n orbital for a system possessing icosahedral symmetry, as given in table 4.4, provide a more interesting and complicated example of the quasispin classification scheme.

It is seen from table 4.4 that the quasispin scheme in this instance does not serve to completely distinguish states, with some terms appearing twice in the classification.⁴

⁴However, as Wybourne noted, this is a substantial improvement on previous schemes, in which terms appeared up to seven times.

A further complication is that of quasispin mixing. For instance, inspection of table 4.4 reveals that there are two 2V terms with $Q = 0, 2$. Therefore the possibility exists for these states to be mixed by the Coulomb interaction operator (which consists of terms of quasispin ranks of 0 and 2 [14]). This situation also occurs in the quasispin classification of the d^5 electronic configuration in $SO(3)$ symmetry (see Wybourne [67]⁵) where two 2D terms exist for $Q = 0, 2$. It is apparent that given these circumstances quasispin does not serve as a good quantum number.

SO(21)	SO(20)	$SU^Q(2) \times Sp(10)$	$SU^S(2) \times SO(5)$	$SU^S(2) \times I$
$\left\{ \begin{array}{c} [\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}] \\ \\ [\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}] \end{array} \right\}$	$\left\{ \begin{array}{c} [\frac{1}{2} \frac{1}{2} \dots \frac{1}{2}] \\ \\ [\frac{1}{2} \frac{1}{2} \dots -\frac{1}{2}] \end{array} \right\}$	$\left\{ \begin{array}{c} {}^6\langle 0 \rangle \\ {}^4\langle 1^2 \rangle \\ {}^2\langle 1^4 \rangle \end{array} \right\}$	$\left\{ \begin{array}{c} {}^1[00] \\ {}^3[11] \\ {}^1[20] \\ {}^5[10] \\ {}^3[21] \\ {}^1[22] \end{array} \right\}$	$\begin{array}{l} {}^1A \\ {}^3(T_1 + T_2 + U') \\ {}^1(U + V + V') \\ {}^5V \\ {}^3(U + U' + V + 2V' + 2T_1 + 2T_2) \\ {}^1(A + A' + 2U + U' + 2V + V' + T_1 + T_2) \end{array}$
		$\left\{ \begin{array}{c} {}^5\langle 1 \rangle \\ {}^3\langle 1^3 \rangle \\ {}^1\langle 1^5 \rangle \end{array} \right\}$	$\left\{ \begin{array}{c} {}^2[10] \\ {}^4[11] \\ {}^2[21] \\ {}^6[00] \\ {}^4[20] \\ {}^2[22] \end{array} \right\}$	$\begin{array}{l} {}^2V \\ {}^4(T_1 + T_2 + U') \\ {}^2(U + U' + V + 2V' + 2T_1 + 2T_2) \\ {}^6A \\ {}^4(U + V + V') \\ {}^2(A + A' + 2U + U' + 2V + V' + T_1 + T_2) \end{array}$

Table 4.4: Icosahedral Symmetry: terms for n electrons in the v orbital in the quasispin scheme. This is an adaptation of Table 7 in Wybourne [65]. Left superscripts denote either $2Q + 1$ or $2S + 1$, where appropriate.

⁵Note that the classification of terms with $Q = 0$ as given in table 7 of this reference is incomplete. Inspection of table 6 reveals that the terms 4DG and 2SDFGI are missing

4.1.5 The Wigner-Eckart theorem and chains of groups

The calculation of group chains is more than just a convenient way of finding a unique way of labelling states. It has an extremely useful application in the calculation of matrix elements.

The Wigner-Eckart theorem can be applied to each group in the chain, relating the reduced matrix elements of a subgroup to a linear combination of the reduced matrix elements of the group next up the chain. That is, if H is a subgroup of G , and T^λ is an irreducible tensor operator, which transforms according to the irreducible representation λ of G , then the reduced matrix element of T^λ for the subgroup H is

$$\langle x_1 \lambda_1 a_1 \sigma_1 | T^{\lambda a \sigma} | x_2 \lambda_2 \sigma_2 \rangle_s^H = \sum_r \begin{pmatrix} \lambda_1 \\ a_1 \\ \sigma \end{pmatrix}_H^G \begin{pmatrix} \lambda_1^* & \lambda & \lambda_2 \\ a_1 & a & a_2 \\ \sigma_1^* & \sigma & \sigma_2 \end{pmatrix}_{sH}^{rG} \langle x_1 \lambda_1 | T^\lambda | x_2 \lambda_2 \rangle_r^G, \quad (4.26)$$

where a is the branching multiplicity of the irreducible representation σ and the labels r and s are used to distinguish the occurrence of λ in the Kronecker product $\lambda_1^* \times \lambda_2$ and σ in $\sigma_1^* \times \sigma_2$ respectively. The label s could include any others needed to distinguish the kets uniquely.

In this way the Wigner-Eckart theorem may be applied throughout a whole group-subgroup chain and the resulting coefficients factorized in the manner described (for more details see Butler [9]). This procedure is commonly referred to as Racah's factorisation lemma. Wybourne points out that many of the coefficients required for the Lie groups in the chain can be found from already existing atomic calculations which use the same chains of Lie groups.

Matrix elements of particular interest are those involving quasispin, for from equation (4.20) these matrix elements will have a dependence on particle number. If a particular interaction is able to be described in terms of a linear combination of irreducible tensor operators, having well defined transformation properties under $SU^Q(2)$, i.e. in terms of Q and M_Q , then these

operators can be written as $T_{M_Q}^{(\alpha Q)}$. The Wigner-Eckart theorem for $SU^Q(2)$ gives

$$\langle \alpha Q M_Q | T_{M_Q}^{(\alpha' Q')} | \alpha'' Q'' M_Q'' \rangle = (-1)^{Q-M_Q} \begin{pmatrix} Q & Q' & Q'' \\ -M_Q & M_Q' & M_Q'' \end{pmatrix} \langle \alpha Q || T^{(\alpha' Q')} || \alpha'' Q'' \rangle. \quad (4.27)$$

As previously mentioned the particle number enters into this equation only through M_Q . Hence the reduced matrix element is entirely free of the particle number and the particle number dependence is held entirely in the $3j$ symbol.

4.1.6 Particle-hole conjugation

Wybourne states certain selection rules which are immediately apparent from equation (4.27).

Selection Rules 4.1.1 Seniority

1. *Matrix elements of quasispin scalars are necessarily diagonal in the seniority number ν , i.e. $\Delta\nu = 0$.*
2. *Matrix elements of irreducible Tensor operators of rank 1 in quasispin must satisfy the seniority selection rule $\Delta\nu = 0, \Delta\nu = \pm 2$.*

Derivations of the selection rules, the relevant $3j$ symbols and the conclusion drawn from them, are given in Figure 4.2.

These selection rules had been known for quite some time. Lawson & MacFarlane [38] and also Watanabe [60] both in 1964, derived such rules from matrix elements classified in the seniority scheme. Wybourne was the first to show their validity in strong crystal fields and in doing so classified matrix elements with quasispin labels. It will be seen in §4.3.9 that the selection rules derived by Ceulemans in 1994 are a specialization of these.

Particle-hole conjugation as previously discussed (see §3.1.1) takes an orbital state of n particles and replaces it with one consisting of $2\lambda - n$ particles. Every single-particle state with an electron gets replaced with an empty state and vice versa. The relationship between matrix

$$\begin{pmatrix} Q & 0 & Q'' \\ -M_Q & 0 & M_Q'' \end{pmatrix} \Rightarrow M_Q = M_Q'' \quad (4.28)$$

$$\begin{pmatrix} Q & 1 & Q'' \\ -M_Q & 1 & M_Q'' \end{pmatrix} \Rightarrow M_Q = 1 + M_Q'' \quad (4.29)$$

$$\Rightarrow \frac{1}{2}(\nu - \lambda) = 1 + \frac{1}{2}(\nu'' - \lambda)$$

$$\Rightarrow \nu = 2 + \nu''$$

$$\begin{pmatrix} Q & 1 & Q'' \\ -M_Q & 0 & M_Q'' \end{pmatrix} \Rightarrow \nu = \nu'' \quad (4.30)$$

$$\begin{pmatrix} Q & 1 & Q'' \\ -M_Q & -1 & M_Q'' \end{pmatrix} \Rightarrow \nu = -2 + \nu'' \quad (4.31)$$

Figure 4.2: Derivation of Selection Rules 4.1.1.

elements in $(\Gamma_a)^n$ and $(\Gamma_a)^{2\lambda-n}$ follows directly from equation (4.27) and a symmetry property of the $3j$ symbol (see Appendix A)

$$\begin{aligned} \langle \alpha Q M_Q | T_0^{(\alpha' Q')} | \alpha'' Q'' M_Q \rangle \\ = (-1)^{(\nu - \nu'')/2 - Q'} \langle \alpha Q - M_Q | T_0^{(\alpha' Q')} | \alpha'' Q'' - M_Q \rangle. \end{aligned} \quad (4.32)$$

From this equation it can be seen that one of the consequences of particle-hole conjugation is to reverse the projection, M_Q , of quasispin.

4.1.7 Example: octahedral group $O \sim S_4$

There are three irreducible representations of the octahedral group, O , with degree $\lambda \geq 2$, E , T_1 and T_2 (in Griffith's notation). Correlations between irreducible representation labels of O

and of S_4 , along with the degree of the representation, $f^{(\mu)}$, are:

$$\begin{array}{ll}
 O \sim T_d \sim S_4 & f^{(\mu)} \\
 A_1 \sim (4) & 1 \\
 T_2 \sim (31) & 3 \\
 E \sim (2^2) & 2 \\
 T_1 \sim (21^2) & 3 \\
 A_2 \sim (1^4) & 1
 \end{array} \tag{4.33}$$

of these only two, $A_1 \sim (4)$ and $T_1 \sim (21^2)$ are unimodular implying that only $T_1 \sim (21^2)$ can be used to induce representations of the unimodular groups $SO(N)$, for $N \geq 2$. A discussion on how to label states in t_2 with quasispin is given in §4.3.2. Since $f^{(21^2)}$ equals 3, (21^2) can induce representations of $SO(3)$. That is the subgroup chain

$$GL(3) \supset SO(3) \supset S_4 \sim O \tag{4.34}$$

can be used.

The method of inner plethysms of S -functions gives the branching rules for $SO(3) \rightarrow O$ (induced by the faithful unimodular irreducible representation $(21^2) \sim T_1$)

$$\begin{aligned}
 (21^2) \otimes [0] &= (4) \\
 (21^2) \otimes [1] &= (21^2) \\
 (21^2) \otimes [2] &= (31) + (2^2) \\
 (21^2) \otimes [3] &= (31) + (21^2) + (1^4) \\
 (21^2) \otimes [4] &= (4) + (31) + (2^2) + (21^2) \\
 (21^2) \otimes [5] &= (31) + (2^2) + 2(21^2) \\
 (21^2) \otimes [6] &= (4) + (14) + (2^2) + (21^2) + 2(31),
 \end{aligned} \tag{4.35}$$

where the numbers in square brackets are irreducible representation labels of $SO(3)$ (corresponding to $l = 0, 1, \dots, 6$). These can be compared with standard results, for example those contained in Griffith [23]. Table 4.5 gives the relevant branching rules.

SO(13)	SO(12)	$SU^Q(2) \times Sp(6)$	$SU^S(2) \times SO(3)$	$SU^S(2) \times O$
$\left[\begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \dots \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \right]$	$\left\{ \begin{array}{l} \left[\begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \dots \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \right] \\ \left[\begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} \dots - \begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \right] \end{array} \right.$	$\left\{ \begin{array}{l} 4\langle 0 \rangle \\ 2\langle 1^2 \rangle \\ 3\langle 1 \rangle \\ 1\langle 1^3 \rangle \end{array} \right.$	$\begin{array}{l} {}^1[0] = {}^1S \\ {}^3[1] = {}^3P \\ \{ {}^1[2] = {}^1D \\ {}^2[1] = {}^2P \\ {}^4[0] = {}^4S \\ \{ {}^2[2] = {}^2D \end{array}$	$\begin{array}{l} {}^1(4) = {}^1A_1 \\ {}^3(21^2) = {}^3T_1 \\ {}^1((31) + (2^2)) = {}^1(T_2 + E) \\ {}^2(21^2) = {}^2T_1 \\ {}^4(4) = {}^4A_1 \\ {}^2((31) + (2^2)) = {}^2(T_2 + E) \end{array}$

Table 4.5: Octahedral Symmetry: terms for n electrons in the t_1 orbitals in the quasispin scheme. Left superscripts denote either $2Q + 1$ or $2S + 1$, where appropriate.

4.1.8 Summary of methodology

In summary, if (μ) is a faithful, unimodular, irreducible representation of S_m and is of degree $f^{(\mu)} = N$, then it is possible to embed S_m in $SO(N)$.

The method of inner plethysms of S -functions may be used to calculate branching rules for $SO(N) \rightarrow S_m$. This is extremely useful because it means it is possible to use irreducible representations of an entire Lie group chain, for example

$$\begin{aligned} U^{(2^\lambda)} \supset SO(4\lambda + 1) \supset SO(4\lambda) \supset SU^Q(2) \\ \times (USp(2\lambda) \supset SU^S(2) \times (O(\lambda) \supset SO(\lambda))), \end{aligned} \quad (4.36)$$

to label the electronic states of the orbital transforming as irreducible representation (μ) of S_m , which is isomorphic to some finite point group (Cayley's Theorem). This means that for the example of §4.1.6, states of t_1^n ($n = 0$ to 6) are uniquely labelled by the group labels

$$|QM_Q SM_S \Gamma_{a\alpha}\rangle. \quad (4.37)$$

4.2 Quasi-Kramers' symmetries

This section examines in full algebraic detail, the 1987 paper of Stedman, "Quasi-Kramers' symmetries under particle-hole conjugation". The driving force behind this paper seems to be to draw analogies between time reversal and its relationship with ordinary spin on the one hand

and particle-hole conjugation and its effect on quasispin on the other. For, with this analogy established, it would not appear to be a very unreasonable expectation that there must exist analogous selection rules for matrix elements of operators with definite parity with respect to particle-hole conjugation just as there is for operators which are time even or time odd in nature.

The first sub-section provides a synopsis of Stedman's paper and simply states the large number of important theorems and results derived by Stedman. The proofs of these are given in Appendix D and 4.2.2.6. These proofs are exclusively algebraic in nature, in marked contrast to Stedman's proofs which were entirely diagrammatic. There are a number of reasons for this, one of the main ones being accessibility — unfortunately diagram techniques in group theory are not widely known or used, unlike the relevant algebra.

The generalized state labelling scheme used in Stedman [56] and also extensively in this and later sections is explained in full detail in Appendix A.1.

It has been found, using the parity arguments outlined in Chapter 2, that several of the properties of Stedman's particle-hole conjugation operator, denoted in this thesis as C_A , as stated by Stedman [56], are not true in all the generality claimed by Stedman. These properties, and the inconsistencies inherent in them, are discussed fully in §4.2.2.6.

At the conclusion of §4.2.2.6 another antilinear particle-hole conjugation operator C'_A is defined and its properties listed. Proofs of these properties are to be found in Appendix C.

4.2.1 Synopsis of Stedman's 1987 paper "Quasi-Kramers' symmetries under particle-hole conjugation".

Stedman [56] defines a "Quasi-spinor" to be $\underline{A}_K \equiv \begin{pmatrix} a_K^\dagger \\ \tilde{a}_K \end{pmatrix}$, where K is the set of labels required to uniquely define the state⁶, a_K^\dagger is the creation operator and $\tilde{a}_K = (KL)a_L$ is the symmetry

⁶The labels K could for instance be equivalent to the ξ labels used by Wybourne [65] (see § 4.1) or simply jm where the symmetry of the system is $SO(3)$. See Appendix A.1 for more details on the state labelling scheme used in this thesis.

adapted annihilation operator. \underline{A}_K is regarded as a “covariant $SU^Q(2)$ spinor” ($Q = \frac{1}{2}$) in quasispin space.

Stedman obtains the generators of the quasispin Lie algebra from coupling (denoted here by the brackets $\left\{ \right.$ and $\left. \right\}$) the components of the “quasi-spinor” \underline{A}_K to an invariant in K labels and to one (1) in quasispin (tensors will be written as T^{KQ} , i.e. with the K labels on the left, quasispin on the right) so that

$$Q(K)_\alpha = \frac{i}{\sqrt{2}} \left\{ \underline{A}_K \underline{A}_L \right\}^{(01)} \quad (4.38)$$

$$= \frac{i}{\sqrt{2}} (KL) A_{Kq} A_{Lq'} \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle. \quad (4.39)$$

Stedman gives a diagram proof that the Q_α^K close under commutation on the $SU^Q(2)$ Lie algebra

$$[Q(K)_\alpha, Q(K)_\beta] = i\varepsilon_{\alpha\beta\gamma} Q(K)_\gamma. \quad (4.40)$$

The explicit form for components of $Q(K)_\alpha$ is given by expansion of equation (4.39) in spherical co-ordinates (using Rotenberg tables) and the conversion to cartesian co-ordinates is made using the contrastandard Fano-Racah transformation.

It is shown by Stedman (using diagrams) that the commutation relations of $\underline{Q}(K)$ and \underline{A}_K are the same as that of orbital angular momentum with spin, i.e. of a rank 1 and a rank $\frac{1}{2}$ tensor.

It is also shown that the quasispin magnitude (equivalent for the maximum $|Q(K)_Z|$) is $\frac{1}{2}$ for states with both states (K and \bar{K}) filled or empty and is zero otherwise (i.e. only one of K and \bar{K} filled) and that Q_+^K and Q_-^K ladder between quasispin states ($Q(K)_+$ fills both K and \bar{K} while $Q(K)_-$ empties).

Quasispin for the entire shell $[2(2l+1)]^N$ is now defined as the summation over all possible

pairs K and \bar{K} ⁷:

$$\underline{Q} = \sum_K \underline{Q}(K) \quad (4.41)$$

$$\Rightarrow Q(K)_Z = \frac{1}{2}((2l+1) - \hat{N}), \quad (4.42)$$

where it should be noted that this is the negative of the result of Wybourne (see §4.1) and \hat{N} is the number operator

$$\hat{N} = \sum_K (a_K^\dagger a_K + a_{\bar{K}}^\dagger a_{\bar{K}}). \quad (4.43)$$

It should also be noted that for a half-filled shell, the eigenvalue M_Q of Q is zero.

Stedman examines other coupled tensors of the \underline{A}_K spinors — ostensibly following Judd [29] except that wherever possible diagram proofs of these are given. The results are

$$\left\{ \underline{A}_K \underline{A}_L \right\}^{(00)} = \delta_{KL} (n(\bar{K}) - n(K) - 1) / \sqrt{2} \quad (4.44)$$

$$\begin{aligned} \left\{ [\underline{A}_K, \underline{A}_{\bar{K}}] \right\}^{(00)} &\equiv \left\{ \underline{A}_K \underline{A}_{\bar{K}} \right\}^{(00)} - \left\{ \underline{A}_{\bar{K}} \underline{A}_K \right\}^{(00)} \\ &= \sqrt{2} (a_{\bar{K}}^\dagger a_{\bar{K}} - a_K^\dagger a_K) \end{aligned} \quad (4.45)$$

$$\left\{ \{ \underline{A}_K, \underline{A}_{\bar{K}} \} \right\}^{(00)} = -\sqrt{2} \quad (4.46)$$

$$\left\{ [\underline{A}_K, \underline{A}_{\bar{K}}] \right\}_\alpha^{(01)} = 0 \quad (4.47)$$

$$\left\{ \{ \underline{A}_K, \underline{A}_{\bar{K}} \} \right\}_\alpha^{(01)} = -(2\sqrt{2}i) Q(K)_\alpha \quad (4.48)$$

$$\begin{aligned} \{ Q(K)_i, Q(K)_j \} &= 2\delta_{ij} (Q(K)_Z)^2 \\ &= \delta_{ij} (1 - n(K) - n(\bar{K}) + 2n(K)n(\bar{K})), \end{aligned} \quad (4.49)$$

where $n(K) = a_K^\dagger a_K$ and so on.

Equation (4.49) is equivalent to the statement that

$$\left\{ \underline{Q}(K) \underline{Q}(K) \right\}^{(02)} = 0 \quad (4.50)$$

⁷It should be noted that an SO(3) nature is implicit in this. In general the number of electronic states is given by $2|\lambda|$, where $|\lambda|$ is the dimension of the irreducible representation λ that the shell transforms as. It should also be noted that in Stedman [56] there exists the implicit assumption that quasispin in situations of reduced symmetry is always a good state label, but this is not always a trivial matter (see §4.1.7 and §4.3.2).

and implies that

$$[\{Q(K)_i, Q(K)_j\}, Q(K)_k] = 0. \quad (4.51)$$

Detailed algebraic proofs of these tensor-coupling relations (4.44)→(4.50) are given in Appendix D.

4.2.1.1 Particle-hole conjugation

After proving (or indicating how to prove) these relations Stedman goes on to define the particle-hole conjugation operator which he denoted simply as “ C ” and shall be referred to in this thesis as “ C_A ”;

$$C = C_L Z = C_A \equiv \left(\prod_K C_K \right) Z \quad (4.52)$$

$$\text{where } C_K = F(K) + G(K) \quad (4.53)$$

$$\text{with } F(K) = n(K)(1 - n(\bar{K})) + n(\bar{K})(1 - n(K)) \quad (4.54)$$

$$\text{and } G(K) = (K\bar{K})(a_{\bar{K}}a_K - a_K^\dagger a_{\bar{K}}^\dagger). \quad (4.55)$$

The explicit, second quantized, definition of C_L had already been given by Keiter et al. in 1969. Stedman was the first to recognise that C_L could be rewritten in terms of quasispin operators, i.e.

$$F(K) = 1 - 4(Q(K)_Z)^2 \quad (4.56)$$

$$\text{and } G(K) = -2iQ(K)_Y. \quad (4.57)$$

In addition, for reasons that will soon be discussed, the operator $C_A = C_L Z$, where Z is the complex conjugation operator was chosen by Stedman to be his definition of a particle-hole conjugation operator. It should be noted, however, that in terms of the discussion in Chapter 2 the definition of $G(K)$ and indeed that of $Q(K)_Y$ are not bipartite. This will be remedied in §4.2.2.6. The properties of C_A , as stated by Stedman [56] are listed in §4.2.2.6 followed by a discussion of each one in turn.

4.2.2 Generalization for point groups

In the process of second quantization, the ket corresponding to a single electronic state uniquely determined by the irreducible representation labels K (K is a composite label and contains, for instance, information about the spatial and spin degrees of freedom) is expressed in terms of a creation operator, carrying the same group-subgroup information as the ket, acting on the “vacuum state” $|0\rangle$;

$$|K\rangle \equiv a_K^\dagger |0\rangle. \quad (4.58)$$

By definition a_K^\dagger is an irreducible tensor operator. The hermitian conjugate of a_K^\dagger is the annihilation operator a_K .

In terms of the diagram techniques used in, for example, Stedman [56, 54] and outlined in full detail in Stedman [57] there strictly must be some method of indicating the “parity” of an operator⁸ (this is discussed in Chapter 2). That is, the annihilation operator a_K could be given positive parity, and the creation operator negative parity. Then in the equations, as in the diagrams, it is only permissible to bring (couple) together two nodes of opposite parity. Coupling nodes of identical parity requires the presence of a parity changing operator.

The $2jm$ symbol is used in this capacity in Stedman [57]. It also has the effect of coupling two nodes to an invariant. In these respects it is not unreasonable to consider the $2jm$ as a metric tensor for angular momenta spaces. To indicate the positive parity of the annihilation operator it could be written as a^K , as for a contragradient tensor component, and to indicate the negative parity of the creation operator the label should be left down — a_K^\dagger — as for a covariant tensor component.

To ensure that a^K transforms as an irreducible tensor operator (as, for example, a_K^\dagger already does) it is necessary to introduce a $2jm$ symbol. As a_K^\dagger has negative parity and a^K positive, strictly speaking, the $2jm$ should indicate this by lowering indices, i.e. $\tilde{a}_K = (KL)^* a^L$ transforms as a_K^\dagger (an irreducible tensor operator).

⁸An example of a “node” in the diagrams of Stedman [57]

While this method would be useful from a “parity housekeeping” point of view, this extra formalism will not be used here for simplicity’s sake and because such keeping track of parities is better suited to diagram techniques (which for accessibility reasons will not be used here, however see Stedman [57]).

4.2.2.1 Quasi-spinors

As discussed above, only with the additional factor of a $2jm$ symbol does the annihilation operator transform as an irreducible tensor operator (for the $SO(3)$ specialisation of this see equation 3.9). The resulting symmetrized operator is denoted by \tilde{a}_K , i.e.

$$\tilde{a}_K = (KL)^* a_L, \quad (4.59)$$

where the $2jm$ has been complex conjugated in order that its labels have negative parity (see Chapter 2). It should be noted that this differs from Stedman [56]. The operators, \tilde{a}_K and a_K^\dagger , transforming, as they do, as irreducible tensor operators of the same rank may be considered as the two components of a rank $\frac{1}{2}$ spinor, A_{Kq} , with $q = \frac{1}{2}, -\frac{1}{2}$. That is

$$A_{K\frac{1}{2}} = a_K^\dagger \quad (4.60)$$

$$\text{and } A_{K-\frac{1}{2}} = \tilde{a}_K. \quad (4.61)$$

4.2.2.2 The effects of hermitian conjugation and of time reversal

The time reversal operator used in this thesis is that used by Wigner [62] and is best described as a symmetrized complex conjugation operator. That is the time reversal operator, T , is comprised of two parts, the complex conjugation operator — denoted by Z — and a unitary matrix U . The requirement that if ψ is an eigenstate of the system, then $T^2\psi$ must also be an eigenstate of the system, leads to the identification of U as the $2jm$ matrix of the group which the system transforms under. For a discussion of the time reversal operator and the properties of U , Wigner [62] Chapter 26 should be consulted, and Chapter 24 of the same book seen for information on the $2jm$ matrix (identified as \mathbf{C} in Wigner and denoted by \mathcal{J} in this thesis) and complex conjugate representations. Appendix A of this thesis contains all the results pertaining

to complex conjugate irreducible representations, the $2jm$ matrix, and the effect of complex conjugation of the $3j$ symbols that are relevant to the formulae in this thesis.

In summary, time reversal is

$$T \equiv UZ, \quad (4.62)$$

where $U \equiv \mathcal{J}$, the $2jm$ matrix, and Z is the complex conjugation operator.

Time reversal and second quantized operators

The effects of time reversal on the creation and annihilation operators a_K^\dagger and a_K are

$$\begin{aligned} \overline{(a_K^\dagger)} &\equiv T a_K^\dagger T^{-1} \\ &= (KL) a_L^\dagger, \end{aligned} \quad (4.63)$$

$$\begin{aligned} \overline{(a_K)} &\equiv T a_K T^{-1} \\ &= (KL)^* a_L. \end{aligned} \quad (4.64)$$

The antilinearity of T produces

$$\begin{aligned} T^2 a_K^\dagger T^{-2} &= (KL)^* (LK') a_{K'}^\dagger \\ &= \{K\} a_K^\dagger \end{aligned} \quad (4.65)$$

$$T^2 a_K T^{-2} = \{K\} a_K. \quad (4.66)$$

It is important to note that the symmetrized annihilation operator \tilde{a}_K is just the same thing as the time reversed operator \bar{a}_K . Denoting time reversed states and operators with an overbar is exceedingly common in the literature (see, for example, Stedman [57]). For this reason the tilde on the symmetrized annihilation operator will be replaced with a bar. Therefore the components of the quasi-spinor A_{Kq} are now written as

$$A_{K\frac{1}{2}} = a_K^\dagger, \quad (4.67)$$

$$\begin{aligned} A_{K\frac{-1}{2}} &= \bar{a}_K \\ &\equiv (KL)^* a_L. \end{aligned} \quad (4.68)$$

Combined hermitian conjugation and time reversal operations

An interesting (and useful) operation is provided by combining the operations of hermitian conjugation and of time reversal, (the hermitian conjugation operator, normally denoted by a dagger is here represented by “ H ”)

$$(HT)A_{K\frac{1}{2}}(HT)^{-1} = A_{K\frac{-1}{2}}, \quad (4.69)$$

$$(HT)A_{K\frac{-1}{2}}(HT)^{-1} = \{K\}A_{K\frac{1}{2}}. \quad (4.70)$$

That is, the action of HT on the quasi-spinor is equivalent to a rotation by π of an ordinary rank $\frac{1}{2}$ tensor (spinor). It is only after four successive applications of HT that the quasi-spinor is returned to its initial state, i.e.

$$(HT)^4 A_{K\frac{1}{2}} (HT)^{-4} = A_{K\frac{1}{2}} \quad (4.71)$$

$$(HT)^4 A_{K\frac{-1}{2}} (HT)^{-4} = A_{K\frac{-1}{2}}. \quad (4.72)$$

This is the same effect as having to rotate a conventional spinor by 4π for it to return to its initial state (see, for example, §56 of Landau & Lifshitz [37] for a discussion of spinors and in particular contravariant and covariant components of these).

In summary \underline{A} is aptly named as a “quasi-spinor” and HT affects rotations by π in some space. It will be shown in the next section that this is a $SU(2)$ space which will be denoted $SU^Q(2)$.

4.2.2.3 Quasispin

The 1973 paper of Wybourne [65] following Sviridov & Smirnov [59] introduced the components of quasispin for crystal fields with no explanation of their derivation (see §4.1 for further details). Following Judd (see Judd [29], Chapter 7) Stedman [56] gives the derivation based on a coupling of the components of the quasi-spinor to rank 1 in quasispin, and to an invariant for the space/spin label K (Judd [29] was $SO(3)$ specific in his definitions, hence K was equivalent to lm_lsm_s in his case).

Following Stedman [56] the components of quasispin are (where, as previously mentioned, the brackets “ $\{$ ” and “ $\}$ ” denote tensor coupling)

$$Q(K)_\alpha \equiv \frac{i}{\sqrt{2}} \{AA\}^{(01)} \quad (4.73)$$

$$\equiv \frac{i}{\sqrt{2}} (KL) \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle A_{Kq} A_{Kq'}, \quad (4.74)$$

where $\langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle$ is a coupling coefficient of $\text{SO}^Q(3) \supset \text{SU}^Q(2)$. It should be noted that the label K , indicating quasispin for a partial single-particle state K is in parentheses, not as an index as in Stedman [56] — this is in agreement with the conventions of Chapter 2. Using the Rotenberg et al. [47] tables, the spherical components of quasispin are

$$Q(K)_1 = (KL) \frac{i}{\sqrt{2}} a_K^\dagger a_L^\dagger \quad (4.75)$$

$$\begin{aligned} Q(K)_0 &= \frac{i}{2} (KL) (a_K^\dagger \bar{a}_L + \bar{a}_K a_L^\dagger) \\ &= \frac{i}{2} (1 + \{K\} a_K^\dagger a_K - a_L^\dagger a_L) \end{aligned} \quad (4.76)$$

$$\begin{aligned} Q(K)_{-1} &= \frac{i}{\sqrt{2}} (KL) \bar{a}_K \bar{a}_L \\ &= \frac{i}{\sqrt{2}} (LK)^* a_L a_K. \end{aligned} \quad (4.77)$$

With this definition the action of hermitian conjugation has the effect:

$$\begin{aligned} HQ(K)_1 H^{-1} &= H \left(\frac{i}{\sqrt{2}} (KL) a_K^\dagger a_L^\dagger \right) H^{-1} \\ &= \frac{-i}{\sqrt{2}} (KL)^* a_L a_K \\ &= \frac{-i}{\sqrt{2}} (LK) \bar{a}_K \bar{a}_L \\ &= -\{K\} Q(K)_{-1} \end{aligned} \quad (4.78)$$

$$\begin{aligned} HQ(K)_0 H^{-1} &= H \left(\frac{i}{2} (1 + \{K\} a_K^\dagger a_K - a_L^\dagger a_L) \right) H^{-1} \\ &= -Q(K)_0 \end{aligned} \quad (4.79)$$

$$\begin{aligned} HQ(K)_{-1} H^{-1} &= H \left(\frac{i}{\sqrt{2}} (LK)^* a_L a_K \right) H^{-1} \\ &= \frac{-i}{\sqrt{2}} (LK) a_K^\dagger a_L^\dagger \\ &= -\{K\} Q(K)_1, \end{aligned} \quad (4.80)$$

where Appendix A should be consulted for an explanation of the $2j$ phase, which has been left in here as $\{K\}$ rather than replacing it with its value of “ -1 ” to maintain the generality of the

results, and as an aid to tracking the various phases in the working.

It is also of interest to determine the behaviour of the spherical components of quasispin with respect to time reversal:

$$\begin{aligned}
 TQ(K)_1T^{-1} &= \frac{-i}{\sqrt{2}}(KL)^*(KL)a_L^\dagger(LK)a_K^\dagger \\
 &= \frac{i}{\sqrt{2}}(LK)a_K^\dagger a_L^\dagger \\
 &= \{K\}Q(K)_1
 \end{aligned} \tag{4.81}$$

$$\begin{aligned}
 TQ(K)_0T^{-1} &= \frac{-i}{2}(1 + \{K\})(KL)(KL)^*a_L^\dagger a_L - (LK)(LK)^*a_K^\dagger a_K \\
 &= \frac{-i}{2}(1 + \{K\})a_L^\dagger a_L - a_K^\dagger a_K \\
 &= \{K\}Q(K)_0 - \frac{i}{2}(1 + \{K\})
 \end{aligned} \tag{4.82}$$

$$\begin{aligned}
 TQ(K)_{-1}T^{-1} &= \frac{-i}{\sqrt{2}}(LK)(LK)^*(KL)^*a_K a_L \\
 &= \frac{i}{\sqrt{2}}(KL)^*a_K a_L
 \end{aligned} \tag{4.83}$$

$$= \{K\}Q(K)_{-1}. \tag{4.84}$$

Again the operation of HT proves to be of interest:

$$(HT)Q(K)_1(HT)^{-1} = -Q(K)_{-1} \tag{4.85}$$

$$(HT)Q(K)_0(HT)^{-1} = -\{K\}Q(K)_0 + \frac{i}{2}(1 + \{K\}) \tag{4.86}$$

$$(HT)Q(K)_{-1}(HT)^{-1} = -Q(K)_1. \tag{4.87}$$

4.2.2.4 Transition to cartesian co-ordinates

Following Stedman [56], and for reasons outlined in Appendix B of Stedman [54], the transition to cartesian co-ordinates is made via the contra-standard (contragradiant-standard) Fano-Racah [18] transformation, where it should be noted that the transformation on page 40 of

Stedman [57] is in error. The transformation is:

$$\begin{pmatrix} Q(K)_x \\ Q(K)_y \\ Q(K)_z \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} i & 0 & -i \\ 1 & 0 & 1 \\ 0 & -i\sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} Q(K)_1 \\ Q(K)_0 \\ Q(K)_{-1} \end{pmatrix} \quad (4.88)$$

giving

$$Q(K)_x = \frac{i}{\sqrt{2}}(Q(K)_1 - Q(K)_{-1}) \quad (4.89)$$

$$Q(K)_y = \frac{1}{\sqrt{2}}(Q(K)_1 + Q(K)_{-1}) \quad (4.90)$$

$$Q(K)_z = -iQ(K)_0. \quad (4.91)$$

Before an explicit form of these operators is given in terms of the basic annihilation and creation operators, the three sets of equations spanning (4.78)→(4.87) may be used to discover the behaviour of the cartesian components of quasispin under the influence of time reversal and hermitian conjugation, both separately and together.

Time reversal gives

$$TQ(K)_xT^{-1} = -\{K\}Q(K)_x \quad (4.92)$$

$$TQ(K)_yT^{-1} = \{K\}Q(K)_y \quad (4.93)$$

$$TQ(K)_zT^{-1} = -\{K\}Q(K)_z + \frac{1}{2}(1 + \{K\}), \quad (4.94)$$

while the operation of hermitian conjugation has the effect:

$$HQ(K)_xH^{-1} = -\{K\}Q(K)_x \quad (4.95)$$

$$HQ(K)_yH^{-1} = -\{K\}Q(K)_y \quad (4.96)$$

$$HQ(K)_zH^{-1} = Q(K)_z. \quad (4.97)$$

The combined action of hermitian conjugation and time reversal represented by the operator HT therefore has the effect on the cartesian components of quasispin of:

$$(HT)Q(K)_x(HT)^{-1} = Q(K)_x \quad (4.98)$$

$$(HT)Q(K)_y(HT)^{-1} = -Q(K)_y \quad (4.99)$$

$$(HT)Q(K)_z(HT)^{-1} = -\{K\}Q(K)_z + \frac{1}{2}(1 + \{K\}). \quad (4.100)$$

These results will be of use later (see §4.2.2.6) with respect to particle-hole conjugation, which as already alluded to in §3.1.5 is in some way related to the operator HT .

The explicit equations for the cartesian components of quasispin are obtained from equations (4.75)→(4.77) and (4.89)→(4.91)

$$Q(K)_x = \frac{-1}{2}(KL)(a_K^\dagger a_L^\dagger - \bar{a}_K \bar{a}_L) \quad (4.101)$$

$$= \frac{-1}{2}((KL)a_K^\dagger a_L^\dagger - (LK)^* a_L a_K)$$

$$Q(K)_y = \frac{i}{2}(KL)(a_K^\dagger a_L^\dagger + \bar{a}_K \bar{a}_L) \quad (4.102)$$

$$= \frac{i}{2}((KL)a_K^\dagger a_L^\dagger + (LK)^* a_L a_K)$$

$$Q(K)_z = \frac{1}{2}(KL)(a_K^\dagger \bar{a}_L + \bar{a}_K a_L^\dagger) \quad (4.103)$$

$$= \frac{1}{2}(\{K\}a_K^\dagger a_K - a_L^\dagger a_L + 1)$$

$$= \frac{1}{2}(\{K\}n(K) - n(L) + 1),$$

where $n(K)$ and $n(L)$ are the number operators for the states K and L respectively, returning 1 if the relevant state is occupied and 0 otherwise. Hence it can be seen that $Q(K)_z$ is simply a variant on the concept of the number operator, its eigenvalue being a simple function of the occupancy of the states K and L ($\equiv \bar{K}$). Naturally $Q(K)_z$ must be hermitian to be a real observable, and it is seen from equation (4.97) that this is indeed the case. If it is also stipulated that $Q(K)_z$ be time even, then it is seen that a requirement for this to be the case is that the $2j$ phase $\{K\}$ must be -1 .

Thus the simple requirement that $Q(K)_z$ be time even has lead to the well known result (see, for

example, Butler [9] §3.2 or Appendix A of this thesis) that the full $2j$ phase $\{K\} = (K\bar{K})(\bar{K}K)^*$ is -1 in any basis for a one electron state in the full chain.

It is now possible to interpret some of the preceding results more fully. Equations (4.95)→(4.97) state that the cartesian components of quasispin are hermitian operators, whilst equations (4.92)→(4.94) state that $Q(K)_x$ and $Q(K)_z$ are time even with $Q(K)_y$ being time odd. Similarly for equations (4.98)→(4.100); $Q(K)_x$ and $Q(K)_z$ are even with respect to the operator HT , $Q(K)_y$ being of odd HT parity.

With the $2j$ phase $\{K\}$ set to -1 it is possible to examine the commutation relations of the spherical components of quasispin. The commutation relations are

$$[Q(K)_{-1}, Q(K)_1] = iQ(K)_0 \quad (4.104)$$

$$[Q(K)_{-1}, Q(K)_0] = -iQ(K)_{-1} \quad (4.105)$$

$$[Q(K)_1, Q(K)_0] = iQ(K)_1. \quad (4.106)$$

See Appendix E for detailed proofs of these. These are algebraic in nature. The reader is referred to Stedman [56] and Stedman [57] for diagrammatic proofs.

Equations (4.104)→(4.106) show that the operators of quasispin close on the $SU(2)$ Lie algebra. To distinguish this algebra from that of spin it shall be denoted $SU^Q(2)$ and the Lie algebra of spin $SU^S(2)$.

4.2.2.5 Particle-hole conjugation

In §3.1.5, in the context of $SO(3)$ symmetry, when the relationship between the particle-hole conjugation operator was being discussed it was pointed out that the combined operator HT was a linear operator whose effect on the single-particle creation and annihilation operators was identical to that corresponding to the linear particle-hole conjugation operator C_L (used, for

example, by Bell [4]). That is

$$C_L a_{jm} C_L^{-1} = (-1)^{j-m} a_{j-m}^\dagger \quad (4.107)$$

$$C_L a_{jm}^\dagger C_L^{-1} = (-1)^{j-m} a_{j-m}. \quad (4.108)$$

In $SO(3)$ the $2j$ symbol $(m\bar{m})$ is real and has values $(-1)^{j-m} \delta_{m-\bar{m}}$. Equations (4.107) and (4.108) may therefore be recast in the form

$$C_L a_{jm} C_L^{-1} = (m\bar{m}) a_{j\bar{m}}^\dagger \quad (4.107')$$

$$C_L a_{jm}^\dagger C_L^{-1} = (m\bar{m})^* a_{j\bar{m}}. \quad (4.108')$$

Therefore, in a consideration of particle-hole conjugation in systems of symmetry other than $SO(3)$, equations (4.107) and (4.108) provide a good starting point, and the operation of HT would seem to be a possible candidate for C_L .

Bell, however, did not consider quasispin and the possible effects particle-hole conjugation would have upon it. Equation 4.32 in §4.1.6 shows that at the very least particle-hole conjugation should reverse the z component of quasispin. That is

$$C_L Q(K)_z C_L^{-1} = -Q(K)_z. \quad (4.109)$$

However, according to equation (4.100) $(HT)Q(K)_z(HT)^{-1} = Q(K)_z$.

So it would appear there is an apparent inconsistency between HT and C_L . The cause of this conflict is identified, however, when the actions of C_L and of HT on operators comprised of two or more annihilation and/or creation operators are considered.

The hermitian conjugation operator takes a ket into a bra and vice-versa

$$(|a\rangle)^\dagger = \langle a| \quad (4.110)$$

in terms of second quantized operators for an arbitrary state

$$(a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger |0\rangle)^\dagger = \langle 0| a_\omega \dots a_\beta a_\alpha. \quad (4.111)$$

That is the effect of hermitian conjugation on an arbitrary string of annihilation and creation operators is to reverse the order of the operators and then to hermitian conjugate each one in turn. This is all very natural behaviour since hermitian conjugation has exactly this same effect on matrices, i.e. complex conjugation transpose.

This simple and well known effect of hermitian conjugation has been emphasised here to contrast with the action of C_L .

There is no inherent re-ordering property of C_L . It is this fact that brings about the inconsistency with the effect of HT . HT and C_L have identical properties when acting on single second quantized operators, but that is not enough to say they are one in the same. The analogy has been useful, however. The correspondence is close enough to replace HT with C_L in equations (4.69)→(4.72) and draw the same conclusions, i.e. C_L rotates the quasi-spinor by π in $SU^Q(2)$,

$$C_L A_{K\frac{1}{2}} C_L^{-1} = A_{K\frac{-1}{2}}, \quad (4.69')$$

$$C_L A_{K\frac{-1}{2}} C_L^{-1} = -A_{K\frac{1}{2}}, \quad (4.70')$$

$$C_L^4 A_{K\frac{1}{2}} C_L^{-4} = A_{K\frac{1}{2}}, \quad (4.71')$$

$$\text{and } C_L^4 A_{K\frac{-1}{2}} C_L^{-4} = A_{K\frac{-1}{2}}, \quad (4.72')$$

where the particle-hole conjugation operator C_L is now defined by equations (4.69') and (4.70') to be that operator which has the effect

$$\begin{aligned} C_L a_K^\dagger C_L^{-1} &= (KL)^* a_L \\ &= \bar{a}_K \end{aligned} \quad (4.112)$$

$$\begin{aligned} C_L a_K C_L^{-1} &= (KL) a_L^\dagger \\ &= \bar{a}_K^\dagger. \end{aligned} \quad (4.113)$$

This is seen to be in perfect agreement with equations (4.107') and (4.108') when the symmetry group is $SO(3)$.

4.2.2.6 The properties of particle-hole conjugation operators

It was mentioned in the previous section that particle-hole conjugation should at the very least reverse the z component of quasispin. Equations (4.112) and (4.113) give the definition of a particle-hole conjugation operator C_L , along with the statements that C_L is linear and unitary (and, of course, has no inherent re-ordering property). It is time to determine the effects of C_L on the cartesian components of quasispin:

$$\begin{aligned}
 C_L Q(K)_x C_L^{-1} &= C_L \frac{-1}{2} ((KL) a_K^\dagger a_L^\dagger - (LK)^* a_L a_K) C_L^{-1} \\
 &= \frac{-1}{2} ((KL) \bar{a}_K \bar{a}_L - (LK)^* \bar{a}_L^\dagger \bar{a}_K^\dagger) \\
 &= \frac{-1}{2} ((LK)^* a_L a_K - (KL) a_K^\dagger a_L^\dagger) \\
 &= -Q(K)_x,
 \end{aligned} \tag{4.114}$$

$$\begin{aligned}
 C_L Q(K)_y C_L^{-1} &= C_L \frac{i}{2} ((KL) a_K^\dagger a_L^\dagger + (LK)^* a_L a_K) C_L^{-1} \\
 &= \frac{i}{2} ((KL) \bar{a}_K \bar{a}_L + (LK)^* \bar{a}_L^\dagger \bar{a}_K^\dagger) \\
 &= \frac{i}{2} ((LK)^* a_L a_K + (KL) a_K^\dagger a_L^\dagger) \\
 &= Q(K)_y,
 \end{aligned} \tag{4.115}$$

$$\begin{aligned}
 C_L Q(K)_z C_L^{-1} &= C_L \frac{1}{2} (1 - a_K^\dagger a_K - a_L^\dagger a_L) C_L^{-1} \\
 &= \frac{1}{2} (1 - \bar{a}_K \bar{a}_K^\dagger - \bar{a}_L \bar{a}_L^\dagger) \\
 &= \frac{1}{2} (1 - a_L a_L^\dagger - a_K a_K^\dagger) \\
 &= \frac{1}{2} (1 - (1 - a_L^\dagger a_L) - (1 - a_K^\dagger a_K)) \\
 &= \frac{1}{2} (a_K^\dagger a_K + a_L^\dagger a_L - 1) \\
 &= -Q(K)_z.
 \end{aligned} \tag{4.116}$$

It can be seen that C_L does indeed have the desired effect on quasispin, i.e. it reverses the z component. It is of interest to note that the x component is also inverted, only $Q(K)_y$ remains unaffected. To “remedy” the situation Judd, in 1967 (see Judd [29]) incorporated the effects of complex conjugation Z into his particle-hole conjugation operator, thus making it antilinear. This operation will be denoted C_A . Its effects on the generalized components of quasispin will

be discussed later in this section.

Stedman attempted to generalize Judd's antilinear particle-hole conjugation operator, which is denoted here by C_A , in order to apply it in situations other than the $SO(3)$ symmetry in which Judd had been working. Unlike Judd, however, who defined C_A for $SO(3)$ in terms of its effect on the second quantized annihilation and creation operators and on the empty and filled shell, Stedman was able to give an explicit expression for C_L , the particle-hole conjugation operator used by, for example, Bell [4]. This was based on the earlier work of Keiter [34]. Stedman's antilinear operator C_A is then the product of the linear operator C_L and complex conjugation Z , i.e. $C_A = C_L Z$.

Remarkably Stedman discovered that the explicit definition of C_L was able to be given in terms of the cartesian components of quasispin. However this definition is not in agreement with the parity considerations of Chapter 2 (or with Stedman's book [57]) and a corrected definition is given here.

$$C_L \equiv \left(\prod_K C(K)_L \right) \quad (4.117)$$

$$\equiv \left(\prod_K [F(K) + G(K)] \right), \quad (4.118)$$

where

$$F(K) = n(K)(1 - n(\bar{K})) + n(\bar{K})(1 - n(K)) \quad (4.119)$$

$$= 1 - 4(Q(K)_z)^2,$$

$$G(K) = (K\bar{K})(\bar{a}_K \bar{a}_{\bar{K}} - a_K^\dagger a_{\bar{K}}^\dagger) \quad (4.120)$$

$$= 2Q(K)_x$$

and the products run over all conjugate pairs $K\bar{K}$. The particle-hole conjugation operator for one such pair is written $C(K)_L$.

Thus Keiter's definition for C_L is expressible in terms of quasispin. Stedman was the first

to write it in this way. Given this explicit definition of C_L in terms of quasispin (and therefore also $C_A = C_L Z$), the properties of C_L are readily determined.

1. C_L is unitary, i.e. $C_L^{-1} = C_L^\dagger$. Also C_L is hermitian ($C_L = C_L^\dagger$) implying that C_L is self inverse, $C_L = C_L^{-1}$
2. C_L toggles empty/filled states
3. C_L has the following effect on the cartesian components of quasispin.

$$C_L \begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix} C_L^{-1} = \begin{pmatrix} -Q_x \\ Q_y \\ -Q_z \end{pmatrix} \quad (4.121)$$

4. C_L and ordinary spin commute
5. $|QM_Q\rangle$ has eigenvalues ± 1 with respect to C_L^2

The proofs of these properties are fairly straightforward and are given in Appendix B.

However, the inclusion of Z in the definition of C_A leads to problems and inconsistencies in the properties of C_A as listed by Stedman. Some of these problems may be overcome by choosing (if possible, Butler [8] hypothesises that this can always be done) the $2jms$ to be real, thus losing some of the generality of the argument. However others can not, such as the fact that property (4) is incorrect, as will be shown. A summary of the (supposed) properties of C_A , as given in Stedman [56], follows.

1. C_A is unitary and antilinear, hence antiunitary.
2. C_A toggles empty/filled states.
3. C_A anticommutes with quasispin.
4. C_A and ordinary spin commute.
5. The states $|QM_Q\rangle$ have eigenvalue ± 1 with respect to C_A^2 .

These properties will now be discussed.

Is C_A antiunitary?

Stedman defines C_A as being antiunitary (antilinear-unitary, as time reversal). The antilinear nature of C_A is obvious as the complex conjugation operator Z is explicitly involved in its definition. The unitary property of C_A is readily proved from the corresponding property of C_L (see Appendix B.1), and is not in question. However the antilinearity proves inconsistent with the next property listed (equation (15) of Stedman).

Does C_A toggle empty/filled states?

The effect of C_A on the annihilation and creation operators is given here in notation consistent with the rest of this thesis:

$$\begin{aligned} C_A a_K^\dagger C_A^{-1} &= \bar{a}_K \\ &= (KL)^* a_L, \end{aligned} \tag{4.122}$$

$$C_A \bar{a}_K C_A^{-1} = -a_K^\dagger. \tag{4.123}$$

These properties are true, for instance, for the linear particle-hole conjugation used by Bell [4]. The requirement of antilinearity imposed by Stedman in his equation (13) makes equation (4.123) inconsistent with equation (4.122).

The first of these equations is acted upon by hermitian conjugation, represented here by the operator H .

$$\begin{aligned} H(C_A a_K^\dagger C_A^{-1})H^{-1} &= \bar{a}_K^\dagger \\ &= (KL)a_L^\dagger. \end{aligned} \tag{4.124}$$

As commented upon early in this section, when acting on single particle states C_L , a linear particle-hole conjugation operator has the same effect on single particle annihilation and creation operators as does the combined operations of hermitian conjugation and time reversal, represented in the operator form as HT . Since the antilinear particle-hole conjugation operator C_A has been derived from the linear C_L by the extra operation of complex conjugation and since

hermitian conjugation and time reversal commute, it follows that C_A will also commute with hermitian conjugation. Therefore equation (4.124) may be written

$$\begin{aligned} C_A a_K C_A^{-1} &= \bar{a}_K^\dagger \\ &= (KL)a_L^\dagger, \end{aligned} \quad (4.125)$$

and hence

$$\begin{aligned} C_A \bar{a}_K C_A^{-1} &= C_A (KL)^* a_L C_A^{-1} \\ &= (KL)(LK)a_K^\dagger, \end{aligned} \quad (4.126)$$

where the last equality follows from the antilinearity of C_A and equation (4.125).

Equation (4.126) can in no way be brought into a form compatible with equation (4.123) (the final of Stedman's equations (15)). In fact, applying the techniques of Chapter 2 it can be seen that equation (4.126) is not a bipartite expression and breaks the "net absolute parity" rule. Using the notation of Chapter 2 to indicate parity

$$\begin{array}{ccccccc} & - & & - & - & + & \\ C_A \bar{a}_K C_A^{-1} & = & C_A (KL)^* a_L C_A^{-1} & = & (KL)(LK)a_K^\dagger & & \end{array} \quad (4.127)$$

This is entirely due to the antilinear property of C_A .

There are three ways in which the inconsistency of equations (4.122) and (4.123) may be overcome:

1. The most simple: the antilinearity of the particle-hole conjugation operator is done away with altogether (a linear particle-hole conjugation operator C_L produces the desired results of equations (4.122) and (4.123)).
2. The condition that C_A commute with hermitian conjugation is relaxed, and instead of equation (4.125) the following is true:

$$\begin{array}{ccc} & + & - - - \\ C_A a_K C_A^{-1} & = & (KL)^* a_L^\dagger. \end{array} \quad (4.125')$$

However it is immediately obvious that this expression is not bipartite and breaks the “net absolute parity” rule. This non-bipartite expression is seen readily enough to satisfy equations (4.122) and (4.123). But for reasons discussed in Chapter 2 this is a less than satisfactory solution.

3. The most obvious: restrictions must be placed on the $2jm$'s to insist that they be real. This is the same conclusion arrived at in the discussion following equations (4.128)→(4.130), and as mentioned in that discussion, was the situation encountered by Judd [29] for the $SO(3)$ case.

A full discussion, involving parity considerations, of why equations (4.122) and (4.123) are not consistent with the definition of C_A being an antilinear particle-hole conjugation operator follows:

Time reversal, hermitian conjugation and complex conjugation are all anti-linear operators, and all reverse parity. C_A is by definition an antilinear operator and yet by equations (4.122) and (4.123) is parity conserving. This leads to algebraic expressions (or indeed, diagrams) which are non-bipartite in structure. As a result restrictions are placed on the $2jms$ involved. Either they must be real or C_A must be such that it has no definite effect upon parity. In the latter case resulting again in non-bipartite, “net absolute parity” breaking expressions.

A linear particle-hole conjugation operator is not only consistent with equations (4.122) and (4.123), but also has the distinction of conserving “net absolute parity” (and maintains bipartite expressions).

Does C_A anticommute with quasispin?

The effects of C_A on the generalized components of quasispin, given by equations (4.101)→(4.101), are readily deduced

$$C_A Q(K)_x C_A^{-1} = \frac{-1}{2}((LK)a_L a_K - (KL)^* a_K^\dagger a_L^\dagger) \quad (4.128)$$

$$C_A Q(K)_y C_A^{-1} = \frac{-i}{2}((LK)a_L a_K + (KL)^* a_K^\dagger a_L^\dagger) \quad (4.129)$$

$$\begin{aligned} C_A Q(K)_z C_A^{-1} &= \frac{1}{2}(a_K^\dagger a_K + a_L^\dagger a_L - 1) \\ &= -Q(K)_z. \end{aligned} \quad (4.130)$$

Two things are immediately obvious. The first is that in the context of Stedman [57] the equations for $Q(K)_x$ and $Q(K)_y$ are no longer bipartite, i.e. it is not possible to transliterate these equations into meaningful diagrams. The second is more striking, an antilinear particle-hole conjugation operator does not, in general close on the operators of quasispin, i.e. it is not possible to write the right-hand side of equations (4.128) and (4.129) in terms of quasispin components. In fact it is only possible to do so if and only if the $2jm$ symbols for the relevant group are real. In which case $(KL) = (KL)^*$ and

$$\begin{aligned} C_A Q(K)_x C_A^{-1} &= \frac{-1}{2}((LK)^* a_L a_K - (KL) a_K^\dagger a_L^\dagger) \\ &= -Q(K)_x \end{aligned} \quad (4.131)$$

$$\begin{aligned} C_A Q(K)_y C_A^{-1} &= \frac{-i}{2}((LK)^* a_L a_K + (KL) a_K^\dagger a_L^\dagger) \\ &= -Q(K)_y \end{aligned} \quad (4.132)$$

$$C_A Q(K)_z C_A^{-1} = -Q(K)_z. \quad (4.133)$$

Stedman [56] was in error on this point. As previously mentioned the $2jm$ symbols of $SO(3)$ are real, hence Judd's result holds for this case.

Do C_A and ordinary spin commute?

According to Landau & Lifshitz [37], the matrices for the components of spin are

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad (4.134)$$

$$\hat{S}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad (4.135)$$

$$\hat{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (4.136)$$

Stedman has $C_A = C_L Z$ and claims that

$$[C_A, \underline{S}] = 0. \quad (4.137)$$

However

$$\{C_A, \hat{S}_y\} = C_L \left\{ Z, \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \right\} = 0, \quad (4.138)$$

which implies that $C_A \hat{S}_y = -\hat{S}_y C_A$. Hence C_A and ordinary spin do not commute. However since \hat{S}_x and \hat{S}_z are real C_A does commute with them.

Does $|QM_Q\rangle$ have eigenvalues of ± 1 with respect to C_A^2 ?

Since $C_A = C_L Z$, and Z commutes with C_L , i.e. $C_L Z = Z C_L$, then

$$C_A^\dagger = (C_L Z)^\dagger = Z C_L^\dagger. \quad (4.139)$$

However C_L is hermitian, hence

$$C_A^\dagger = Z C_L = C_L Z = C_A, \quad (4.140)$$

i.e. C_A is hermitian also. Then necessarily

$$(C_A)^2 = C_A C_A^\dagger \quad (4.141)$$

$$= (C_L Z)(C_L Z)^\dagger \quad (4.142)$$

$$= C_L Z Z C_L^\dagger \quad (4.143)$$

$$= C_L C_L^\dagger \quad (4.144)$$

$$= (C_L)^2. \quad (4.145)$$

Hence from the corresponding property for C_L (see Appendix B.5) the eigenvalues of $(C_A)^2$ are ± 1 on $|QM_Q\rangle$.

The definition of C'_A

At this point it would seem that an antilinear particle-hole conjugation operator is not able to be constructed in such a way as to maintain biparticity (or equivalently maintain “net absolute parity”), let alone reverse the cartesian components of quasispin. If, however, the defining equations (4.122) and (4.123) are replaced with simply:

$$C'_A a_K^\dagger C'^{-1}_A = -a_K \quad (4.146)$$

$$C'_A a_K C'^{-1}_A = -a_K^\dagger. \quad (4.147)$$

Then these and the statements that the C'_A is antilinear, unitary and completely fills the empty shell (and empties the filled shell), satisfies these requirements.

Actually it is readily verified that the operator combination $C_L T$ also produces the effect of equations (4.146) and (4.147). This then will be taken to be the definition of C'_A , i.e.

$$C'_A \equiv C_L T. \quad (4.148)$$

A complete list of the properties of C'_A follows.

1. C'_A is unitary, i.e. $C'^{-1}_A = C'^\dagger_A$. Also C'_A is hermitian ($C'_A = C'^\dagger_A$) implying that C'_A is self inverse, $C'_A = C'^{-1}_A$. In addition, since C'_A is also antilinear it is referred to as being anti-unitary (as for time reversal)

2. C'_A toggles empty/filled states
3. C'_A anticommutes with quasispin.

$$C'_A \begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix} C'^{-1}_A = - \begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix} \quad (4.149)$$

4. C'_A and ordinary spin anticommute (also anticommutes with orbital angular momentum, when it is defined)
5. $|QM_Q\rangle$ has eigenvalues ± 1 with respect to C'^2_A

Proofs of these properties are in Appendix C.

It is also immediately obvious that C'_A reverses parity, as is befitting an antilinear operator. The effect of C'_A on the cartesian components of quasispin (property (3) above) is not much more difficult to determine:

$$\begin{aligned}
& \begin{matrix} 0 & & & + + & - - & & - - & + + \end{matrix} \\
C'_A Q(K)_x C'^{-1}_A &= C'_A \left[\frac{-1}{2} ((KL)a_K^\dagger a_L^\dagger - (LK)^* a_L a_K) \right] C'^{-1}_A \\
& \begin{matrix} & & - - & + + & & + + & - - \end{matrix} \\
&= \frac{-1}{2} ((KL)^* a_K a_L - (LK)a_L^\dagger a_K^\dagger) \\
& \begin{matrix} 0 \end{matrix} \\
&= -Q(K)_x
\end{aligned} \quad (4.150)$$

$$\begin{aligned}
& \begin{matrix} 0 & & & + + & - - & & - - & + + \end{matrix} \\
C'_A Q(K)_y C'^{-1}_A &= C'_A \left[\frac{i}{2} ((KL)a_K^\dagger a_K^\dagger + (LK)^* a_L a_K) \right] C'^{-1}_A \\
& \begin{matrix} & & - - & + + & & - - & + + \end{matrix} \\
&= \frac{-i}{2} ((KL)^* a_K a_L + (LK)a_L^\dagger a_K^\dagger) \\
& \begin{matrix} 0 \end{matrix} \\
&= -Q(K)_y
\end{aligned} \quad (4.151)$$

$$\begin{aligned}
& \begin{matrix} 0 & & + - & & - + \end{matrix} \\
C'_A Q(K)_z C'^{-1}_A &= C'_A \left[\frac{1}{2} (a_L a_L^\dagger - a_K^\dagger a_K) \right] C'^{-1}_A \\
&= \begin{matrix} & - + & & + - & \\ \frac{1}{2} (a_L^\dagger a_L - a_K a_K^\dagger) & & & & \end{matrix} \\
&= \begin{matrix} & + - & & - + & \\ \frac{1}{2} ((1 - a_L a_L^\dagger) - (1 - a_K^\dagger a_K)) & & & & \end{matrix} \tag{4.152} \\
&= \begin{matrix} & + - & & - + & \\ \frac{-1}{2} (a_L a_L^\dagger - a_K^\dagger a_K) & & & & \end{matrix} \\
&= \begin{matrix} 0 \\ -Q(K)_z \end{matrix}
\end{aligned}$$

It will be shown in §4.3.4 that C'_A is equivalent to the operator $O(\varphi)$, developed by Ceulemans [12] by a very different method than that which has so far been used in this thesis. It is quite startling to note that Ceulemans certainly had no notion of quasispin whatsoever when he developed $O(\varphi)$ and the fact that it reverses quasispin is quite an unexpected result.

With C'_A taken to be the standard (anti-linear) particle-hole conjugation operator the following statement may be made in full generality:

Particle-hole conjugation is to quasispin as time reversal is to ordinary spin.

As Stedman pointed out in the introduction to his 1987 paper “Quasi-Kramers symmetries under particle-hole conjugation”:

We anticipate selection rules of analogous form for various quantities and arising from the algebra of quasispin and the particle-hole conjugation.

These selection rules do transpire from Ceulemans’ $O(\varphi)$ and the implications are very far reaching. In particular, as will be discussed in detail in §4.3.8.2 a consequence of the Ceulemans’ selection rules is that (Ceulemans [12])

“The implication is that isolated half-filled shell states cannot exhibit

first-order Jahn-Teller activity''

4.3 Ceulemans' approach and selection rules for half-filled ligands and shells

This section begins with synopses of two papers written by Arnout Ceulemans, but separated by a period of ten years. In both of these papers Ceulemans derived selection rules for half-filled shell states, but by dramatically different methods. Therefore it is the purpose of this section to reconcile the methodologies of these two papers.

This is begun in §4.3.3, with an example of the type of formalism Ceulemans was using in 1984. This example is based on the definition of particle-hole conjugate ligand states contained in Sugano et al. [50]. This example provides an indication of how the particle-hole conjugation operator $O(\varphi)$ used by Ceulemans in 1984 is related to the linear particle-hole conjugation operator C_L , given explicit definition in §4.2.2.6, and consequently to C'_A .

The properties of $O(\varphi)$ and of C'_A are listed in §4.3.4 and a formal equivalence is drawn between them.

In his 1994 paper Ceulemans dealt with states which were distinguished by, amongst other things, quasispin labels. He did not, however, consider the effects of a particle-hole conjugation operator of any sort on these states. This is done in §4.3.5, where in particular, the similarities between C'_A and T on half-filled shells is shown.

That there exists two distinct type of half-filled shell has been known and been discussed in the literature for quite some time (see Griffith [23] and Judd & Runciman [33]). However Ceulemans [12] claimed to have for the first time a group theoretical explanation for why this should be so. His arguments are reproduced in §4.3.6 in terms of C_L .

§4.3.7 consists of four parts. In each part a consideration of the effect of one of the operators of hermitian conjugation, time reversal, linear particle-hole conjugation or antilinear particle-hole conjugation on the primitive, unit single-particle irreducible-tensor operators is given. The results from this section prove vital to the next.

A reproduction of the derivation of Ceulemans' 1984 selection rules in terms of second-quantized operators is given in §4.3.8. Because of the equivalence of $O(\varphi)$ and C'_A (shown in §4.3.4), the by now well known properties of C'_A (in particular the fact that $C'_A \equiv C_{LT}$) are shown to lead directly to the same conclusions drawn by Ceulemans. The implications of which are discussed in §4.3.8.2.

The discussion of Ceulemans' 1994 paper, begun in §4.3.2, is concluded in §4.3.9 with the derivation of the 1994 version of Ceulemans' selection rules, which are phrased in terms of the "quasispin character" of the states.

Connections between the 1984 and the 1994 versions of the rules are elucidated in §4.3.10. This is made fairly straightforward by a simple rephrasing of the statements relating to the relationship between the quasispin character of a single-particle operator and its parity with respect to time reversal.

4.3.1 Synopsis of Ceulemans' 1984 paper "Molecular symmetry and the theory of transition metal ions"

Ceulemans' 1984 paper "Molecular symmetry and the theory of transition metal ions" (Ceulemans [12]) is largely a review of some of the (then current) assumptions, techniques and tools for quantum inorganic chemistry (ligand field theory).

Most of the development is based on standard texts that most solid state physicists would be familiar with, for example Sugano et al. [50], Griffith [23, 24], Fano & Racah [18] and so on.

The one major detraction in this paper is the reliance on the method of matrices and determinants, in particular Laplace's expansion of the determinant in terms of complementary minors, for all the major theorems to do with particle-hole conjugation.

For that is the essence of the original material in this paper, to generalize the concepts of particle-hole conjugation as developed by, for example Sugano et al. [50] and Griffith [23] for the specific case of d^n electrons which are split by an octahedral symmetry field.

Eventually selection rules for half-filled ligand shells are obtained which are shown to have repercussions for the Jahn-Teller effect (these selection rules are the main topic of interest for this section of the thesis). However, as mentioned above, the methods used by Ceulemans, while mathematically precise, and certainly not in question, tend to be too mathematically exhausting to be truly satisfying.

Therefore it is the intention of §4.3.8 to rederive the aforementioned selection rules using the techniques of second-quantization. The hope is to make the development that much more transparent, and acceptable to most physicists and also to be better able to see the connection with other authors in the field of particle-hole conjugation; such as Stedman [56], Wybourne [65] and, surprisingly enough, Ceulemans [13] himself.

4.3.2 Synopsis of Ceulemans' 1994 paper "Electronic and vibronic spectra of transition metal complexes I"

This section is intended to be a brief introduction and synopsis of Chapter 2 of Ceulemans 1994 paper (Ceulemans [13]). It is in particular a description of the methods used, and assumptions made, by Ceulemans in deriving a set of selection rules for half-filled ligand shells — rules that bear a remarkable resemblance to the Ceulemans 1984 set of selection rules. The precise connection between the two sets of rules will be outlined in §4.3.10 — it is necessary to emphasize at this point, however, that the connection was not made by Ceulemans himself, but as far as the author knows, is original to this thesis.

At first glance the 1984 and 1994 papers of Ceulemans appear to be dramatically different. The 1984 paper used a methodology which was in the tradition of Sugano et al. [50] and Griffith [23], i.e. the formalism of Slater determinants was used to describe multi-electronic states in ligand-field theory. On the other hand the 1994 paper followed more in the traditions of the atomic spectroscopists. A second quantized ligand-field theoretic approach was used in lieu of Slater determinants, thus encapsulating the Pauli exclusion principle in the anticommutation relations of annihilation and creation generators, rather than in mathematics corresponding to permutations of rows and columns of determinants.

Another new addition in the 1994 paper was the appearance of quasispin and, following from that, an adaptation of Judd's triple tensor concept (see Judd [29]). In fact it is through the concept of quasispin, as a label for states, and also for the single-particle, interaction operators, that Ceulemans developed his new derivation of selection rules for half-filled ligand states.

4.3.2.1 State labelling scheme

It will be recalled from §3.2.3.1 that Judd's triple tensor notation defined annihilation and creation operators in situations of $SO(3)$ symmetry. Tensor ranks of Q for quasispin, S for spin, and L for orbital angular momentum were assigned to the creation and symmetry adapted annihilation operators. Therefore there were two far from non-trivial difficulties Ceulemans had to overcome in order to use this formalism.

1. What is the corresponding concept of orbital angular momentum of $SO(3)$ theory for ligand states?
2. When is it possible to label ligand states (and hence the second quantized operators) with definite quasispin rank Q ?

Actually it is found that the above two questions are subject to the same problem and hence are answered by the same solution.

For the specific problem which Ceulemans dealt with in his 1994 paper (which was the case of the d^n electrons of Cr(III) complexes being split by the octahedral symmetry of the potential field) it is found that the d^n electrons transforming as the five dimensional irreducible representation $\mathbf{2}$ of $SO(3)$ (using Butler [9] notation) form the multiplets which are labelled e_g and t_{2g} (see equation (4.35)), since they transform as the irreducible representations E (of dimension two) and T_2 (of dimension three) of the octahedral group respectively.

Ceulemans considered the case of the t_2 ligand and made use of the fact that the three spin orbitals for the t_2 shell are isomorphic to the spin orbitals for the atomic p^n configurations (see, for example, Griffith [23] §9.5). However difficulties arise since the matrices corresponding to rotations in $SO(3)$, which give rise to orbital angular momentum, are unimodular and unfortunately this is not the case for t_2 (not all the matrices representing group operations have determinant +1).

These difficulties are overcome by Ceulemans through making use of the fact that

$$T_2 = A_2 \times T_1. \quad (4.153)$$

Therefore it is always possible to convert the T_2 basis to a T_1 basis (and vice versa) for which the group matrices are unimodular and for which the so called "pseudo angular momentum" labelling scheme is valid.

But the fact that the irreducible representation matrices of t_2 are not all unimodular was just the problem encountered in §4.1.7 when discussing the validity of the quasispin labelling scheme for this shell.

Therefore Ceulemans' solution to question (1) also provides the answer to question (2). When the change is made from the T_2 to the T_1 basis, both quasispin Q and (via the $t_2^n \sim p^n$ isomorphism) "pseudo angular momentum" L are good irreducible representation labels, and may be used to distinguish states.

Thus the state labelling scheme in Ceulemans' 1994 paper for electronic configurations in the t_{2g} shell is

$$|QM_QSM_SLM_LM_\Gamma\rangle, \quad (4.154)$$

where M_Γ is a label referring to one of the three basis functions of the T_2 irreducible representation. That is, the states are uniquely specified by no less than seven labels. It is via this state labelling scheme that Ceulemans derives his 1994 version of selection rules for half-filled shells.

Ceulemans gives in his Table 3 a depiction of his quasispin classification scheme of the $(t_{2g})^n$ shell as $n = 0$ to 6. Although this scheme is derived by more conventional methods (character tables) than the one derived in §4.1.7 of this thesis, and outlined in Table 4.5, it is quickly verified that the two schemes agree.

4.3.2.2 Quasispin and triple tensor notation

Quasispin labels are thus amongst those distinguishing states, and will therefore also appear as labels on the second-quantized annihilation and creation operators. In a similar manner to that described in §3.2.3.1, these second quantized operators may be considered to be “triple tensors” (see Judd [29] for the original definition) and may be coupled together to form other operators of definite quasispin rank. Thus Ceulemans coupled the creation triple tensor operators, $a_{\frac{1}{2}m_s m_l}^{(\frac{1}{2}s l)} \equiv a_{m_s m_l}^\dagger$, and the symmetry adapted annihilation operators $a_{-\frac{1}{2}m_s m_l}^{(\frac{+1}{2}s l)} \equiv \tilde{a}_{m_s m_l}$ ($= (-1)^{s+l-m_s-m_l} a_{-m_s -m_l}$), together to form bilinear products⁹ which had total M_Q value of zero¹⁰. Obviously the bilinear product operators thus formed will also have total M_S and M_L values of zero as well, i.e. will be scalars in the spin and orbital angular momentum spaces.

The coupling of two quasispin rank half tensors will form operators of either rank 0 (a quasispin singlet) or of rank 1 (a quasispin triplet) in total quasispin.

⁹An example of such a bilinear product is the z component of quasispin itself, for example see equation (3.100) or (4.103)

¹⁰See §3.2.3 for a definition of the labelling scheme

Ceulemans was interested in such bilinear product operators since, owing to the fact that they consist of the product of an annihilation operator with a creation operator, they describe a single-particle interaction. In fact, as Ceulemans demonstrated, any arbitrary single-particle interaction may be described in terms of bilinear products of this form. Two different expressions were obtained, depending as to whether or not the interaction operator was time even or time odd. Denoting the single particle interaction operator as \mathcal{H} , which has the second quantized definition $\mathcal{H} = \sum_{\zeta\eta} a_{\zeta}^{\dagger} \mathcal{H}_{\zeta\eta} a_{\eta}$, where the composite labels $\zeta \equiv (m_{s_{\zeta}}, m_{l_{\zeta}})$ and $\eta = (m_{s_{\eta}}, m_{l_{\eta}})$ have been used to label the constituent annihilation and creation operators, Ceulemans obtained

1. for \mathcal{H} time even (i.e. $T\mathcal{H}T^{-1} = \tau_{\mathcal{H}}\mathcal{H} = +\mathcal{H}$)

$$\mathcal{H} = \frac{1}{2} \sum_{\zeta} \mathcal{H}_{\zeta\zeta} + \frac{1}{2} \sum_{\zeta\eta} (-1)^{-s-l-m_{s_{\eta}}-m_{l_{\eta}}} \mathcal{H}_{\zeta\eta} (a_{\zeta}^{\dagger} \tilde{a}_{-\eta} + \tilde{a}_{\zeta} a_{-\eta}^{\dagger}). \quad (4.155)$$

The first summation term is readily identified as the expectation value of \mathcal{H} , it is therefore real and scalar, i.e. it must be of zero rank in Q , S and L . Its matrix elements will appear on the main diagonal. The second term corresponds to a quasispin triplet — it is symmetric under the exchange of the quasi-spinors a_{ζ}^{\dagger} for \tilde{a}_{ζ} and $\tilde{a}_{-\eta}$ for $a_{-\eta}^{\dagger}$ — its elements appear on the off diagonal of the interaction matrix.

2. for \mathcal{H} time odd (i.e. $T\mathcal{H}T^{-1} = \tau_{\mathcal{H}}\mathcal{H} = -\mathcal{H}$)

$$\mathcal{H} = \frac{1}{2} \sum_{\zeta\eta} (-1)^{-s-l-m_{s_{\eta}}-m_{l_{\eta}}} \mathcal{H}_{\zeta\eta} (a_{\zeta}^{\dagger} \tilde{a}_{-\eta} - \tilde{a}_{\zeta} a_{-\eta}^{\dagger}). \quad (4.156)$$

Since the summation is antisymmetric under the exchange of a_{ζ}^{\dagger} for \tilde{a}_{ζ} and $\tilde{a}_{-\eta}$ for $a_{-\eta}^{\dagger}$, the operator corresponds to rank 0 in quasispin, i.e. it is a quasispin singlet.

It is now clearly seen that single-particle irreducible-tensor operators of rank 1 in quasispin are time even and that operators of rank 0 in quasispin are time odd. It was through this relationship that Ceulemans derived the selection rules for half-filled shell states that will be discussed in §4.3.9.

4.3.3 Particle-hole conjugation in ligand fields

The approach taken by Ceulemans [12] to particle-hole conjugation in ligand-field theory is largely based on the example of particle-hole conjugation for d^n electrons split by an octahedral

field into the e_g and t_{2g} ligands, as discussed by Sugano et al. [50] and Griffith [23]. Ceulemans' approach was to attempt to encapsulate in an operator all the required properties and effects of an exchange of particles and holes.

In this introductory section, particle-hole conjugation as per Sugano et al. is examined. The effects of the other particle-hole conjugation operators are also explored.

Particle-hole conjugation, in general terms an exchange of filled and empty spin orbitals, is defined in Sugano et al. [50] equation (4.16)

$$\psi(t_2^6 {}^1A_1) = q^{-\frac{1}{2}} \sum_{\substack{S\Gamma \\ M_S M_\Gamma}} (-1)^{S-M_S} \psi(t_2^n S\Gamma M_S M_\Gamma) \hat{\psi}(t_2^{6-n} S\Gamma - M_S M_\Gamma) \quad (\text{Sugano 4.16})$$

i.e. complementary states are defined in such a way as to couple to the invariant 1A_1 state (the filled shell). Equation (4.16) of Sugano et al. stems from their equation (4.12)

$$\begin{aligned} \psi(t_2^6 {}^1A_1) = q^{-\frac{1}{2}} \sum_{\substack{S\Gamma \\ M_S M_\Gamma}} \alpha_{S\Gamma} \langle SM_S S - M_S | 00 \rangle \langle \Gamma M_\Gamma \Gamma M_\Gamma | A_1 e_1 \rangle \\ \times \psi(t_2^n S\Gamma M_S M_\Gamma) \hat{\psi}(t_2^{6-n} S\Gamma - M_S M_\Gamma), \end{aligned} \quad (\text{Sugano 4.12})$$

where $\alpha_{S\Gamma}$ is determined so that $\hat{\psi}(t_2^{6-n} S\Gamma - M_S M_\Gamma)$ is normalized, i.e.

$$|\alpha_{S\Gamma} \langle SM_S S - M_S | 00 \rangle \langle \Gamma M_\Gamma \Gamma M_\Gamma | A_1 e_1 \rangle|^2 = 1. \quad (\text{Sugano 4.13})$$

The values of the Clebsch-Gordan coefficients appearing in this equation are

$$\langle SM_S S - M_S | 00 \rangle = (-1)^{S-M_S} (2S+1)^{-\frac{1}{2}} \quad (\text{Sugano 4.14a})$$

and

$$\langle \Gamma M_\Gamma \Gamma M_\Gamma | A_1 e_1 \rangle = (\Gamma)^{-\frac{1}{2}} \epsilon_\Gamma, \quad (\text{Sugano 4.14b})$$

where (Γ) is the dimension of irreducible representation Γ and ϵ_Γ is a conventional phase factor such that

$$\epsilon_\Gamma^2 = 1.$$

(Sugano 4.13) is *satisfied* if $\alpha_{S\Gamma}$ is

$$\alpha_{S\Gamma} \equiv \epsilon_{\Gamma}[(2S+1)(\Gamma)]^{\frac{1}{2}}. \quad (\text{Sugano 4.15})$$

It should be noted that this is equivalent to saying that the $2jm$ symbols should be being used in (Sugano 4.12), i.e.

$$\langle SM_S S - M_S | 00 \rangle \rightarrow (S\bar{S}) \equiv (-1)^{S-M_S} \quad (4.157)$$

$$\langle \Gamma M_{\Gamma} \Gamma M_{\Gamma} | A_1 e_1 \rangle \rightarrow (\Gamma\bar{\Gamma}) \equiv \epsilon_{\Gamma}. \quad (4.158)$$

This implies that in the specific case considered by Sugano et al. (d^n electrons in an octahedral field) that the $2jm$ symbol $(\Gamma\bar{\Gamma})$ is *real* and has value ± 1 .

With respect to this specific case in Sugano et al. Ceulemans' particle-hole conjugation operator $O(\varphi)$, which will be defined more fully in §4.3.4, is that operator which has the effect

$$O(\varphi)\psi(t_2^n S\Gamma M_S M_{\Gamma})O(\varphi)^{-1} = (-1)^{S-M_S} \hat{\psi}(t_2^{6-n} S\Gamma - M_S M_{\Gamma}), \quad (4.159)$$

while the linear particle-hole conjugation operator C_L , defined in §3.1.1–3.1.2 and generalized in §4.2.2.2 has the effect

$$C_L\psi(t_2^n S\Gamma M_S M_{\Gamma})C_L^{-1} = \hat{\psi}(t_2^{6-n} S\Gamma M_S M_{\Gamma}), \quad (4.160)$$

i.e. $O(\varphi)$ reverses the spin projection M_S and C_L does not.

Bearing in mind that the basis functions M_{Γ} are real (in this example), the effect of Wigner's time reversal T is

$$T\psi(t_2^n S\Gamma + M_S M_{\Gamma})T^{-1} = (-1)^{S-M_S} \psi(t_2^n S\Gamma - M_S M_{\Gamma}) \quad (4.161)$$

hence

$$(TC_L)\psi(t_2^n S\Gamma M_S M_{\Gamma})(TC_L)^{-1} = (-1)^{S-M_S} \hat{\psi}(t_2^{6-n} S\Gamma - M_S M_{\Gamma}). \quad (4.162)$$

It follows that the effect of C_L , followed by T on the wavefunctions ψ for this specific example is equivalent to the effect of $O(\psi)$, i.e.

$$TC_L \equiv O(\varphi). \quad (4.163)$$

Conversely it is implied that

$$TO(\varphi) = (-1)^{2(S-M_S)}C_L. \quad (4.164)$$

That is to say the effect of $O(\varphi)$ followed by time reversal, is to within a phase the same thing as a linear particle-hole conjugation operation.

It is emphasized that the above development is just an example — the assumption is d^n electrons in an octahedral splitting field. There are real $2jms$ ($\Gamma\bar{\Gamma}$) $\equiv \epsilon_\Gamma$, and also real basis functions M_Γ . It serves the purpose at this early stage, however, of showing the relationship between these three very important operators, which will be explored more fully later in this section.

4.3.4 The connection between $O(\varphi)$ and C'_A

In this section the properties of Ceulemans' antiunitary particle-hole conjugation operator $O(\varphi)$ and of C'_A — the “corrected” antiunitary particle-hole conjugation operator of §4.2.2.6 are listed and compared. Based on this comparison a general statement is made about their equivalence. According to Ceulemans:

1. $O(\varphi)$ is *defined* solely for the half-filled shell.
2. $O(\varphi)$ is *defined* as an antilinear operator.
3. $O(\varphi)^2$ has eigenvalue $+1$ (-1) if the number of electrons in the half-filled ligand shell is even (odd).
4. Half-filled shell states connected by $O(\varphi)$ transform contragradiently (by the complex conjugated, irreducible representation matrices).
5. $O(\varphi)$ commutes with spatial symmetry operations.

6. As expected, as a particle-hole conjugation operator, $O(\varphi)$ exchanges particles and holes, thus filling the empty shell and vice versa.

On the other hand the C'_A operator defined in §4.2.2.6 has the following properties:

1. C'_A is antilinear.
2. $(C'_A)^2$ has eigenvalues of ± 1 for half-filled shells (ligand or otherwise).
3. C'_A is unitary ($C_A'^{\dagger} = C_A'^{-1}$).
4. C'_A has the following effect on annihilation/creation operators

$$C'_A a_K^{\dagger} C_A'^{-1} = -a_K \quad (4.165)$$

$$C'_A a_K C_A'^{-1} = -a_K^{\dagger}, \quad (4.166)$$

which are equivalent to hermitian conjugation for isolated operators. Thus $C'_A \equiv C_L T$.

5. C'_A reverses \underline{Q} , \underline{S} and \underline{L} . That is

$$\{C'_A, \underline{Q}\} = \{C'_A, \underline{S}\} = \{C'_A, \underline{L}\} = 0. \quad (4.167)$$

6. C'_A takes the irreducible representation Γ into its conjugate $\bar{\Gamma}$

$$(\Gamma(G) \times \bar{\Gamma}(G) = 0(G)), \quad (4.168)$$

where Butler [9] notation has been used to denote the invariant of the group G as $0(G)$.

7. C'_A fills the empty shell and empties the filled shell

$$C'_A |0\rangle = \left(\prod_K (K \bar{K}) a_K^{\dagger} a_{\bar{K}}^{\dagger} \right) |0\rangle \equiv |C\rangle \quad (4.169)$$

$$C'_A |C\rangle = |0\rangle. \quad (4.170)$$

8. If ket $|b\rangle = C'_A |a\rangle$, where $|a\rangle$ and $|b\rangle$ are half-filled shells. Then $|b\rangle$ transforms contragradiently to $|a\rangle$, with respect to spatial operations. This is really just a restatement of property (6).

Therefore, based on these lists of properties it is possible to make the statement:

$O(\varphi)$ is equivalent of C'_A to within a phase.

4.3.5 The effect of C_L, T and C'_A on states labelled in the quasispin scheme

For states labelled in the scheme of, for example, Ceulemans [13], C_L and T have the following effects:

$$C_L|QM_QSM_SLM_LM_\Gamma\rangle = (-1)^{Q-M_Q}|Q-M_QSM_SLM_LM_\Gamma\rangle \quad (4.171)$$

$$T|QM_QSM_SLM_LM_\Gamma\rangle = (-1)^{S+L-M_S-M_L}(\Gamma\bar{\Gamma})|QM_QS-M_SL-M_L\bar{M}_\Gamma\rangle, \quad (4.172)$$

where $(\Gamma\bar{\Gamma})$ is the $2jm$ symbol for irreducible representation Γ of group G (in this case the octahedral group, but this will be kept general) and the effect of C_L on quasispin labels is discussed in Appendix B.

This implies that the effect of T on the half-filled shell gives

$$T|Q0SM_SLM_LM_\Gamma\rangle = (-1)^{S+L-M_S-M_L}(\Gamma\bar{\Gamma})|Q0S-M_SL-M_L\bar{M}_\Gamma\rangle \quad (4.173)$$

and C_L gives

$$C_L|Q0SM_SLM_LM_\Gamma\rangle = (-1)^Q|Q0SM_SLM_LM_\Gamma\rangle. \quad (4.174)$$

Using the result $C'_A = C_L T = T C_L$ it can then be seen that

$$C'_A|Q0SM_SLM_LM_\Gamma\rangle = (-1)^{Q+S+L-M_S-M_L-M_Q}(\Gamma\bar{\Gamma})|Q0S-M_SL-M_L\bar{M}_\Gamma\rangle \quad (4.175)$$

and also

$$T^2|Q0SM_SLM_LM_\Gamma\rangle = (-1)^{2(S+L)}\{\Gamma\}|Q0SM_SLM_LM_\Gamma\rangle. \quad (4.176)$$

The similarity between C'_A and T on half-filled shells (equations (4.173) and (4.175)) should be noted — they are identical to within a phase.

This example strengthens the identification of C'_A as $O(\varphi)$, the particle-hole conjugation operator for half-filled shells defined by Ceulemans, where Ceulemans $O(\varphi)$ is characterized by the properties listed in §4.3.4. Ceulemans states that $O(\varphi)$ shares properties number (2, 3, 4 and 5) with time reversal (and consequently with C'_A).

4.3.6 The two types of half-filled shell

Ceulemans [12] constructs a projection operator from the operator $O(\varphi)$ and the time reversal operator T (Ceulemans uses Wigner's original notation, $O(\theta)$, for time reversal).

To do this he first obtains the commutation relations for $O(\varphi)$ and T for half-filled shells, i.e.

$$O(\varphi)T = |\mathbf{T}|^{-1}TO(\varphi), \quad (4.177)$$

where $|\mathbf{T}|$ is the determinant of the matrix representation of T . It should be noted that the matrix \mathbf{T} is just the $2jm$ matrix \mathcal{J} with elements on the skew diagonal being the $2jm$ symbols (KL) in row K and column L . For a spin orbital (spin up spin down) and a suitable normalization choice (see Butler [9]) the matrix $\mathbf{T} \equiv \mathcal{J}$ is just

$$\begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}, \quad (4.178)$$

which has determinant +1, i.e. is unimodular (closely related to product of $2j$ phases).

Since $O(\varphi)T \equiv C'_AT \equiv C_LT^2 = C_L\{K\}$ it is obtained that for a half-filled shell,

$$C_LT^2 = (-1)^Q(-1)^{2(S+L)}\{\Gamma\}. \quad (4.179)$$

A similar result is obtained for $TO(\varphi) \equiv TC_LT = \overline{C}_LT^2 = \overline{C}_L\{K\}$, in that it is possible to show that to within a phase $O(\varphi)T$, which is equivalent to C_L , is its own inverse and hence generates a group of dimension two. This group, according to Ceulemans, must contain two irreducible representations both of singular dimension, i.e. the totally symmetric A_1 and the totally antisymmetric A_2 irreducible representations (1 and $\tilde{1}$ in Butler's notation).

Using this fact, symmetry adapted basis functions are constructed using the projection operator

$$\mathcal{A}^\pm = 1 \pm |\mathbf{T}|^{\frac{1}{2}}O(\varphi)T, \quad (4.180)$$

where $|\mathbf{T}|^{\frac{1}{2}}$ is the square root of the determinant of the matrix representation of T — time reversal — and as previously mentioned is related to the product of $2j$ phases.

This means that to within a phase

$$\mathcal{A}^{\pm} = 1 \pm C_L. \quad (4.181)$$

Since from Appendix B.1 it is known that $C_L = C_L^{\dagger} = C_L^{-1}$, following Ceulemans' argument it can be said that is the generator for an Abelian group of order two, which has two irreducible representations $\mathbf{1}$ and $\tilde{\mathbf{1}}$.

According to Ceulemans this gives a group theoretical justification for the two types of half-filled shell (mentioned in, for example, Griffith [23] and Judd & Runciman [33]). The other way of looking at these two types of half-filled shell is that C_L has eigenvalue ± 1 on the half-filled shell.

4.3.7 The effect of H, T, C_L and C'_A on irreducible-tensor, single-particle operators

The results contained in this section are of paramount importance in the new derivation of Ceulemans' selection rules outlined in §4.3.8.

4.3.7.1 The effect of H on $U_m^M(aK, a'L, r)$

In second quantized notation, a single-particle irreducible-tensor operator $V_m^M(aK, a'L, r)$ is written

$$V_m^M(aK, a'L, r) = \sum_{KL} a_K^{\dagger} a_L v_{kml}^{KML}, \quad (4.182)$$

where, by the Wigner-Eckart theorem¹¹ (or rule JLV3 in Stedman [57]), the coefficients v_{kml}^{KML} are proportional to vector coupling coefficients. This constant of proportionality is known as a reduced matrix element, i.e.

$$v_{kml}^{KML} = \langle aK || V^{Mr} || a'L \rangle (K \bar{K}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r. \quad (4.183)$$

¹¹For more information on the Wigner-Eckart theorem expressed for point groups see Butler [9] Chapter 4.

Hence the coefficients v_{kml}^{KML} have the symmetry properties¹²

$$v_{\bar{k}\bar{m}\bar{l}}^{\bar{K}\bar{M}\bar{L}} = \langle a\bar{K} | V^{\bar{M}r} | a'\bar{L} \rangle (\bar{K}K) \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r \quad (4.184)$$

$$= \frac{\langle a\bar{K} | V^{\bar{M}r} | a'\bar{L} \rangle}{\langle aK | V^{Mr} | aL \rangle^*} \{K\} (M\bar{M})^* (v_{kml}^{KML})^* \quad (4.185)$$

$$v_{l\bar{m}k}^{LMK} = \frac{\langle a'L | V^{Mr} | aK \rangle}{\langle a\bar{K} | V^{\bar{M}r} | a'\bar{L} \rangle} (L\bar{L}) (K\bar{K})^* \{\bar{L}MKr\} v_{\bar{k}\bar{m}\bar{l}}^{\bar{K}\bar{M}\bar{L}} \quad (4.186)$$

The unit tensor operators are irreducible-tensor operators with reduced matrix elements of unity. They are a valid choice to use as a basis in order to express any arbitrary tensor operator as a linear combination of, since they are linearly independent. Attention is restricted to these for simplicity's sake.

Hence the definition of unit tensor single-particle operator $U_m^M(aK, a'L, r)$ is

$$U_m^M(aK, a'L, r) = \sum_{KL} a_K^\dagger a_L (K\bar{K}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (4.187)$$

and the effect of hermitian conjugation H upon U_m^M is

$$(U_m^M(aK, a'L, r))^\dagger = \sum_{KL} a_L^\dagger a_K (K\bar{K})^* (\bar{K}K) (M\bar{M}) (L\bar{L}) \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r \quad (4.188)$$

$$= \{K\} \{\bar{K}MLr\} (M\bar{M}) \sum_{KL} a_L^\dagger a_K (L\bar{L}) \begin{pmatrix} \bar{L} & \bar{M} & K \\ \bar{l} & \bar{m} & k \end{pmatrix}^r \quad (4.189)$$

$$= \{K\} \{\bar{K}MLr\} (M\bar{M}) U_{\bar{m}}^{\bar{M}}(a'L, aK, r). \quad (4.190)$$

¹²See Appendix A for more on the symmetry properties of the $2jm$ and $3jm$ symbols

4.3.7.2 The effect of T on $U_m^M(aK, a'L, r)$

In a similar manner to the previous section, the effects of time reversal T on a unit tensor operator $U_m^M(aK, a'L, r)$ may be discovered.

$$T(U_m^M(aK, a'L, r))T^{-1} = \sum_{KL} (K\bar{K}) a_{\bar{K}}^\dagger (L\bar{L})^* a_L^\dagger (K\bar{K})^* (\bar{K}K) (M\bar{M}) (L\bar{L}) \quad (4.191)$$

$$\times \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r$$

$$= \sum_{KL} a_{\bar{K}}^\dagger a_{\bar{L}} (M\bar{M}) (\bar{K}K) \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r \quad (4.192)$$

$$= (M\bar{M}) U_{\bar{m}}^{\bar{M}}(a\bar{K}, a'\bar{L}, r). \quad (4.193)$$

If $V_m^M(aK, a'L, r)$ is a physical operator then it must be hermitian ($V^\dagger = V$). If in addition V has a definite time reversal signature ($TVT^{-1} \equiv \bar{V} = \tau_V V$) then upon expansion of V_m^M in terms of the unit tensor operators U_m^M , and using the linear independence property of the unit tensor operators, equations (4.190) and (4.193) may be coupled together to show that the diagonal reduced matrix elements have the property

$$\langle aK || V_{\bar{m}}^{\bar{M}} || aK \rangle = \tau_V \{K\} \{K\bar{M}\bar{K}r\} \langle aK || V_{\bar{m}}^{\bar{M}} || aK \rangle \quad (4.194)$$

and hence must vanish whenever

$$\tau_V \{K\} \{K\bar{M}\bar{K}r\} = -1. \quad (4.195)$$

However the comment on page 82 of Stedman [57] indicates that as M_r (the r th occurrence of M) in $K \times K$ is in $[K \times K]_\pm$ (the symmetric or antisymmetric square) the $3j$ phase $\{K\bar{M}\bar{K}r\}$ is ± 1 respectively. This may be summarized as

$$M_r \in [K \times K]_{\{K\bar{M}\bar{K}r\}}. \quad (4.196)$$

Hence the restriction (equation (4.195)) of the $3j$ phase may be expressed as

$$\bar{M}_r \in [K \times K]_{\tau_V \{K\}}. \quad (4.197)$$

This is Stedman's statement of the time reversal selection rule (Stedman [57] page 97).

4.3.7.3 The effect of C_L on $U_m^M(aK, a'L, r)$

The linear particle-hole conjugation operator C_L has the following effect on the annihilation and creation operators (see equations (4.112) and (4.113))

$$C_L a_K^\dagger C_L^{-1} = (K\bar{K})^* a_{\bar{K}} \quad (4.198)$$

$$C_L a_K C_L^{-1} = (K\bar{K}) a_{\bar{K}}^\dagger. \quad (4.199)$$

Thus the effect of C_L on U_m^M is

$$C_L U_m^M(aK, a'L, r) C_L^{-1} = \sum_{KL} (K\bar{K})^* a_{\bar{K}}(L\bar{L}) a_L^\dagger (K\bar{K}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (4.200)$$

$$= \sum_{KL} a_{\bar{K}} a_L^\dagger (L\bar{L}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (4.201)$$

$$= \sum_{KL} (\delta_{\bar{K}\bar{L}} - a_L^\dagger a_{\bar{K}}) (L\bar{L}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (4.202)$$

$$= \{\bar{K}MLr\} \left(\sum_K (K\bar{K}) \begin{pmatrix} K & M & \bar{K} \\ k & m & \bar{k} \end{pmatrix}^r - \sum_{KL} a_L^\dagger a_{\bar{K}} (L\bar{L}) \begin{pmatrix} L & M & \bar{K} \\ l & m & \bar{k} \end{pmatrix}^r \right). \quad (4.203)$$

The final term in equation (4.203) may be further simplified

$$\begin{aligned} & \{\bar{K}MLr\} \sum_{KL} a_L^\dagger a_{\bar{K}} (L\bar{L}) \begin{pmatrix} L & M & \bar{K} \\ l & m & \bar{k} \end{pmatrix}^r \\ &= \{\bar{K}MLr\} \{L\} \sum_{KL} a_L^\dagger a_{\bar{K}} (\bar{L}L) \begin{pmatrix} L & M & \bar{K} \\ l & m & \bar{k} \end{pmatrix}^r \end{aligned} \quad (4.204)$$

$$= \{\bar{K}MLr\} \{L\} U_m^M(a'\bar{L}, a\bar{K}, r), \quad (4.205)$$

however, from equation (4.189) it is found that

$$\begin{aligned} \{K\}\{L\}(\overline{M}M)^* \left[U_{\overline{m}}^{\overline{M}}(a\overline{K}, a'\overline{L}, r) \right]^\dagger \\ = \{L\}\{\overline{K}MLr\} \sum_{KL} a_L^\dagger a_{\overline{K}}(\overline{L}L) \begin{pmatrix} L & M & \overline{K} \\ l & m & \overline{k} \end{pmatrix}^r \end{aligned} \quad (4.206)$$

$$= \{L\}\{\overline{K}MLr\} U_m^M(a'\overline{L}, a\overline{K}, r). \quad (4.207)$$

The left-hand side of the above equation may be simplified via the quasi-ambivalence property of the $3jm$ symbol (see Appendix A). This implies

$$(M\overline{M})^* \left[U_{\overline{m}}^{\overline{M}}(a\overline{K}, a'\overline{L}, r) \right]^\dagger = \{L\}\{\overline{K}MLr\} U_m^M(a'\overline{L}, a\overline{K}, r). \quad (4.208)$$

Hence equation (4.203) can now be written

$$\begin{aligned} C_L \left[U_m^M(aK, a'L, r) \right] C_L^{-1} &= \{\overline{K}MLr\} \sum_K (K\overline{K}) \begin{pmatrix} K & M & \overline{K} \\ k & m & \overline{k} \end{pmatrix}^r \\ &- (M\overline{M})^* \left[U_{\overline{m}}^{\overline{M}}(a\overline{K}, a'\overline{L}, r) \right]^\dagger. \end{aligned} \quad (4.209)$$

4.3.7.4 The effect of C'_A on $U_m^M(aK, a'L, r)$

It is now wished to determine what effect the antilinear particle-hole conjugation operator of Ceulemans [12] has upon the unit, single-particle, irreducible-tensor operators $U_m^M(aK, a'L, r)$.

$O(\varphi)$ has been found to be equivalent (to within a phase) to the operator C'_A , for which the effects on the second-quantized operators — a_K^\dagger, a_K — are

$$C'_A a_K^\dagger C'^{-1}_A = -a_K, \quad (4.210)$$

$$C'_A a_K C'^{-1}_A = -a_K^\dagger. \quad (4.211)$$

It is also now known that C'_A is a composite operator consisting of the product of the particle-hole conjugation operator C_L and time reversal T .

Therefore in determining the effects of C'_A on U_m^M there are two possible approaches. Either

operate directly on the constituent components of U_m^M , or combine the previously determined effects of C_L and of T on U_m^M (equations (4.209) and (4.193) respectively).

For the sake of thoroughness the first approach will be taken.

$$C'_A U_m^M(aK, a'L, r) C'^{-1}_A = \sum_{KL} a_K a_L^\dagger (K\bar{K})^* \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^{*r} \quad (4.212)$$

$$= \sum_{KL} (\delta_{KL} - a_L^\dagger a_K) (K\bar{K})^* (\bar{K}K) (M\bar{M}) (L\bar{L}) \quad (4.213)$$

$$\times \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r$$

$$= \sum_K \{K\} (M\bar{M}) (K\bar{K}) \begin{pmatrix} K & M & \bar{K} \\ k & m & \bar{k} \end{pmatrix}^r \quad (4.214)$$

$$- \sum_{KL} \{K\} (M\bar{M}) a_L^\dagger a_K (L\bar{L}) \begin{pmatrix} \bar{L} & \bar{M} & K \\ \bar{l} & \bar{m} & k \end{pmatrix}^r \{ \bar{K} M L r \}$$

$$= \langle U_m^M \rangle - \{K\} \{ \bar{K} M L r \} (M\bar{M}) U_m^{\bar{M}}(a'\bar{L}, a\bar{K}, r) \quad (4.215)$$

$$= \langle U_m^M \rangle - [U_m^M(aK, a'L, r)]^\dagger, \quad (4.216)$$

where $\langle U_m^M \rangle$ is the expectation value of U_m^M in the closed shell and $[U_m^M(aK, a'L, r)]^\dagger$ is the hermitian conjugate of $U_m^M(aK, a'L, r)$, an expression for which can be found in equations (4.188)→(4.190).

Since $\langle U_m^M \rangle$ is an expectation value it is obviously real, hence equation (4.216) can be found to be in perfect agreement with the combination of equations (4.209) and (4.193).

4.3.8 The Ceulemans' 1984 selection rules for half-filled shell states

In a very similar vein to the time reversal selection rule as stated by Stedman (Stedman [57] page 97, and see equation (4.197)), the Ceulemans' selection rules for half-filled shell states are a set of very simple, broad statements with remarkably wide ranging application and influence.

Paraphrasing the words of Ceulemans: the special configurational symmetry of the half-filled

shell also affects the interaction matrix elements. In the case of a one-electron hermitian operator \mathcal{H}_m^M , one has the following

Selection Rules 4.3.1 Ceulemans 1984

1. *Interaction elements between half-filled shell states of opposite (C_L) parity will be zero if \mathcal{H}_m^M is antisymmetric under time reversal.*
2. *Off-diagonal interaction elements between half-filled shell states of identical (C_L) parity will be zero if \mathcal{H}_m^M is symmetric under time reversal.*
3. *Diagonal interaction elements between half-filled shell states will be zero if \mathcal{H}_m^M is symmetric under time reversal and not totally symmetric under the spatial symmetry operations.*

The proof of these rules follows directly from equation (4.216) and the composite nature of the antilinear particle-hole conjugation operator of Ceulemans — $O(\varphi)$, which, it is emphasized here again, is equivalent to within a phase to $C'_A = C_L T$. It is an interesting point to note that this means that these rules stem from not just a linear choice of particle-hole conjugation operator, nor from just the antilinear choice, but from the effects of both separately and together.

4.3.8.1 A new derivation of Ceulemans' selection rules

The action of C'_A on a half-filled shell state distinguished by the (composite) irreducible representation label K is denoted by

$$C'_A |K\rangle \equiv \widetilde{|\overline{K}\rangle} \quad (4.217)$$

and similarly for the ket $|K\rangle$.

In addition, the time reversed kets (and bras) will be denoted by a bar

$$T|K\rangle = \overline{|\widetilde{K}\rangle}, \quad (4.218)$$

where it should be noted that both the bar and the tilde are over the entire ket — not just the irreducible representation label(s).

The composite nature of C'_A (and the fact that C_L and T commute) allows equation (4.217) to

be written

$$\widetilde{|K\rangle} = TC_L|K\rangle = \pi_K \overline{|K\rangle}, \quad (4.219)$$

where π_K is the eigenvalue of C_L for the half-filled shell and has values of ± 1 . Similarly the parity of C_L for the ket $|L\rangle$ is denoted π_L .

Therefore matrix elements of the operator \mathcal{H}_m^M in the “complementary” space due to the particle-hole conjugation have the following property

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \pi_K \pi_L \overline{\langle K | \mathcal{H}_m^M | L \rangle}. \quad (4.220)$$

The operator \mathcal{H}_m^M , being a single particle tensor operator, may be expanded as a linear combination with the unit tensor operators as a basis. It follows from the antiunitary nature of C'_A ($\equiv O(\varphi)$) and equation (4.216) that

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \langle K | \tilde{\mathcal{H}}_m^M | L \rangle^* \quad (4.221)$$

$$= \langle K | L \rangle^* \langle \mathcal{H}_m^M \rangle - \langle K | \mathcal{H}_m^{M\dagger} | L \rangle^*, \quad (4.222)$$

where the notation $\tilde{\mathcal{H}}_m^M$ has been used to denote the action of C'_A on $\mathcal{H}_m^M - C'_A \mathcal{H}_m^M C'^{-1}_A$, and $\langle \mathcal{H}_m^M \rangle$ represents the expectation value of \mathcal{H}_m^M in the closed shell.

By hypothesis \mathcal{H}_m^M is a hermitian operator (has real observable eigenvalues) hence

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \langle L | K \rangle \langle \mathcal{H}_m^M \rangle - \langle L | \mathcal{H}_m^M | K \rangle, \quad (4.223)$$

which relates the matrix elements of \mathcal{H}_m^M in the complementary space of particle-hole conjugation to those in the non-conjugate space.

From equation (4.220), the fact that time reversal is antiunitary, and the assumption that the operator \mathcal{H}_m^M has definite time reversal parity, $\tau_{\mathcal{H}^M}$, it is found that

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \pi_K \pi_L \overline{\langle K | \mathcal{H}_m^M | L \rangle} \quad (4.224)$$

$$= \pi_K \pi_L \langle K | \overline{\mathcal{H}}_m^M | L \rangle^* \quad (4.225)$$

$$= \pi_K \pi_L \tau_{\mathcal{H}^M} \langle L | \mathcal{H}_m^M | K \rangle, \quad (4.226)$$

where $\overline{\mathcal{H}}_m^M = T\mathcal{H}_m^M T^{-1} = \tau_{\mathcal{H}^M} \mathcal{H}_m^M$.

The selection rules now follows through combination of equations (4.223) and (4.226)

$$\pi_K \pi_L \tau_{\mathcal{H}^M} \langle L | \mathcal{H}_m^M | K \rangle = \langle L | K \rangle \langle \mathcal{H}_m^M \rangle - \langle L | \mathcal{H}_m^M | K \rangle. \quad (4.227)$$

This is equivalent to equation (73) of Ceulemans 1984, with $p = \pi_K \pi_L$ and $q = \tau_{\mathcal{H}^M}$.

There are three cases to consider corresponding to the three selection rules:

1. The interaction occurs between half-filled shell states $|K\rangle$ and $|L\rangle$ which possess different parities with respect to $C_L = \pi_K$ and π_L respectively. This implies that necessarily the configurations are different, i.e. $|K\rangle \neq |L\rangle$, and also that the product of parities $\pi_K \pi_L$ has the value -1 . The hypothesis that \mathcal{H}_m^M is antisymmetric under time reversal is represented in equation (4.227) by setting $\tau_{\mathcal{H}^M} = -1$. It follows that the interaction matrix element $\langle L | \mathcal{H}_m^M | K \rangle$ must vanish if these criteria are met.
2. The interaction occurs between half-filled shell states $|K\rangle$ and $|L\rangle$ with identical C_L parities, i.e. $\pi_K \pi_L = +1$. This does not necessarily imply, however, that the states themselves be identical. Off diagonal interaction elements are considered so that even in the case of an interaction occurring between identical states the matrix elements with value $\langle \mathcal{H}_m^M \rangle$ need not be considered.

Further, if it is hypothesised that \mathcal{H}_m^M be symmetric under time reversal ($\tau_{\mathcal{H}^M} = +1$) then it follows from equation (4.227) that the off diagonal matrix elements must necessarily vanish.

3. The diagonal matrix elements between half-filled shell states are now considered. If it is assumed that the interaction operator \mathcal{H}_m^M is symmetric under time reversal (also as in case (2)), then $\tau_{\mathcal{H}^M} = +1$.

The diagonal interaction elements are just the expectation value of \mathcal{H}_m^M in the closed

shell, which is zero if \mathcal{H}_m^M is not totally symmetric under spatial operations¹³, but obviously has time reversal parity +1. It now follows that if the above criteria are met then the diagonal matrix elements must vanish.

4.3.8.2 Implications of Ceulemans' selection rules

Certainly the most far reaching effect of these three, simply stated, rules follows from statement (3).

Since a linear Jahn-Teller interaction corresponds to an operator which is symmetric under time reversal ($\tau_{\mathcal{H}^M} = +1$), but not totally symmetric under spatial symmetry operations. It therefore follows that

Linear Jahn-Teller interaction elements between half-filled shell states of the same C_L parity are forbidden.

This is the case for any isolated half-filled shell state.

In an earlier paper Ceulemans [11] discussed particle-hole exchange symmetry in organic molecules. In particular he used the group-theoretical implications of the particle-hole conjugation operator to offer a reason why, for instance, the Jahn-Teller theorem is “violated” by the $|^1E'\rangle$ wavefunctions for planar Trimethylene-methane — as reported by Borden [7] in 1976. In fact Borden was of the opinion that this lack of Jahn-Teller activity was an indication that the $|^1E'\rangle$ wavefunctions were not the correct ones. Ceulemans was able to refute this hypothesis with an argument based on the fact that the molecular wavefunctions in equation were of e^2 symmetry (half-filled e ligands) and thus fall into the general category covered by the selection rules.

Further experimental verification of the absence of (expected) Jahn-Teller activity in transition metal ion complexes is discussed at length by Ceulemans et al. [15]. For example, mention is made of some very accurate experimental observations which suggest the complete absence of

¹³ Another way of saying this is that $\langle \mathcal{H}_m^M \rangle$ vanishes if $M_r \notin [K \times K]_{\{KMK_r\}}$

the linear (first-order) Jahn-Teller effect in the excited ${}^2E_g(t_{2g}^3)$ state of Cr(III) complexes. It is also commented upon that “no detailed explanation of these remarkable observations appears to be available in the literature”. This thesis offers a generalized development of Ceulemans' selection rules including any explanation for such phenomena.

4.3.9 The Ceulemans' 1994 selection rules for half-filled shell states

Perhaps realising the general inelegance of his method to derive his selection rules for half-filled shell states (which involved lengthy calculations based on the Laplace expansion of Slater determinants), in 1994 Ceulemans published an alternative derivation of these rules (Ceulemans [13] or §4.3.2 for a synopsis of the paper). This new derivation was based on the much more widely understood (and accepted) methods of second quantization. Through the isomorphism of the t_{2g}^n states with the atomic p^n orbitals (see, for example, Griffith [23]), quasispin of the (pseudo) SO(3) variety was introduced. The general statement of the selection rules now involved mention of the “quasispin character” of half-filled states.

The rules are:

Selection Rules 4.3.2 Ceulemans 1994

1. *Interaction elements between half-filled shell states with different quasispin character will be zero for time odd one-election operators.*
2. *Off-diagonal elements between half-filled shell states with identical quasispin character will be zero for time-even one-election operators.*
3. *Diagonal interaction elements will be zero for time-even one-election operators that are not totally symmetric scalars in spin and orbit space.*

The similarity of these rules with Ceulemans' rules of ten years previously (Selection Rules 4.3.1) is striking. In fact if the phrase “quasispin character” is replaced with the word “parity” (with respect to C_L) they are identical. The precise nature of the relationship between the formalisms escaped Ceulemans, however. This will be discussed in §4.3.10, but first a brief description of

the development of these rules is needed.

Wybourne in 1991 (Wybourne [67]) following Judd [29] showed how any interaction may be expanded as a linear combination of operators of well defined quasispin. In fact these tensors for $SO(3)$ will have three labels, K for quasispin, κ for ordinary spin and k for orbital angular momentum. Thus the tensor is referred to as a triple tensor

$$X_{\pi\sigma\tau}^{(K\kappa k)}. \quad (4.228)$$

The Wigner-Eckart theorem for such a triple tensor placed between states of well defined quasispin is now

$$\begin{aligned} \langle \alpha Q M_Q | X_{\pi\sigma\tau}^{(K\kappa k)} | \alpha' Q' M'_Q \rangle = \\ (-1)^{Q-M_Q} \begin{pmatrix} Q & K & Q' \\ -M_Q & \pi & M'_Q \end{pmatrix} \langle \alpha Q || X_{\sigma\tau}^{(K\kappa k)} || \alpha' Q' \rangle. \end{aligned} \quad (4.229)$$

Using the symmetry property (3c) in Appendix A.3.1 and setting the projection π of K equal to zero (as is appropriate for operators corresponding to single particle interactions) it follows that

$$\begin{aligned} \langle \alpha Q M_Q | X_{0\sigma\tau}^{(K\kappa k)} | \alpha' Q' M'_Q \rangle = \\ (-1)^{Q+K+Q'-2M_Q} \langle \alpha Q - M_Q | X_{0\sigma\tau}^{(K\kappa k)} | \alpha' Q' - M'_Q \rangle. \end{aligned} \quad (4.230)$$

In particular, for a half-filled shell state, $M_Q = 0$ and the interaction matrix element must vanish unless

$$(-1)^{Q+K+Q'} = +1, \quad (4.231)$$

i.e. unless

$$Q + K + Q' \text{ is even.} \quad (4.232)$$

This result then is the governing result for Ceulemans' selection rules¹⁴.

¹⁴Actually it is interesting to note that equation (4.231) is simply a statement of quasispin ambivalence for $SO^Q(3)$ and half-filled shells

As mentioned in §4.3.2 Ceulemans, via a method of re-expressing the generic second-quantized expression for the one-electron tensor operator in terms of quasispin operators, was able to draw a correlation between the quasispin rank of an operator, and its behaviour under time reversal.

1. The operator is time even. The operator corresponds to a quasispin triplet, i.e. it has quasispin rank $K = 1$. The operator consists of two parts, the first of which is proportional to the trace of the operator matrix, the second is a symmetric function giving the off diagonal terms.
2. The operator is time odd. The operator corresponds to a quasispin singlet, i.e. it has quasispin rank $K = 0$. The operator is an antisymmetric function giving only off diagonal terms.

The interaction matrix element, of an operator of rank K in quasispin between states of definite quasispin ranks Q and Q' , is proportional to the $3j$ symbol

$$\begin{pmatrix} Q & K & Q' \\ -M_Q & \pi & M_Q \end{pmatrix}. \quad (4.233)$$

This is a consequence of the Wigner-Eckart theorem and this property was used, for example, by Wybourne [67]. The $3j$ symbol (4.233) is subject to the usual triangle conditions (see Appendix A equation (A.20))

$$|Q - K| \leq Q + K. \quad (4.234)$$

If attention is restricted to those interactions which are scalar in quasispin, this implies that $\pi = 0$. Ceulemans showed that this is the case for single-particle iteration operators.

Further, if attention is restricted to those shells which are half-filled then $M_Q = 0$, and the $3j$ symbol of interest is

$$\begin{pmatrix} Q & K & Q' \\ 0 & 0 & 0 \end{pmatrix}. \quad (4.235)$$

The triangle condition of equation (4.234), together with the requirement that $Q + K + Q'$ be even impose very strict conditions on the $3j$ symbol for it not to vanish. For the two possible values of K (corresponding to the time evenness or oddness of the interaction), these imply for a time odd operator

$$K = 0 : \quad \Delta Q = 0. \quad (4.236)$$

and for a time even operator

$$K = 1 : \quad \Delta Q = \pm 1. \quad (4.237)$$

As in the previous statement of Ceulemans' selection rules (see §4.3.8.1) there are three cases

1. The interaction occurs between half-filled shell states with different quasispin character ($Q \neq Q'$). If the interaction is time odd in nature then it will have quasispin rank $K = 0$. However by equation (4.236) above this is a contradiction, the interaction matrix element must vanish.
2. The interaction occurs between half-filled shell states with identical quasispin character ($\Delta Q = 0$). If the interaction is time even then it has quasispin rank $K = 1$. It follows from equation (4.237) above that off diagonal interaction matrix elements must vanish.
3. The interaction is time even ($K = 1$). From the fact that necessarily $K \in [Q \times Q]_{\{QKQ\}}$ and the requirement that $\{QKQ\} = +1$ the diagonal matrix elements will vanish if the interaction is not a totally symmetric scalar in spin and orbital angular momenta.

4.3.10 The connection between Ceulemans' 1984 and 1994 selection rules

The previous section highlights a remarkable feat by Arnout Ceulemans. He was able to, over the time interval of ten years, derive essentially the same selection rules twice by two dramatically different methods.

The only thing more remarkable than this achievement was the fact that since the methods

used in each case were so different, Ceulemans was unable to reconcile the relationship between the two formalisms¹⁵. The connection is in fact, beautiful in its simplicity.

The 1984 derivation relied upon the eigenvalues of a linear particle-hole conjugation operator. An operator that was both hermitian and unitary, i.e. was equal to its own inverse. This operator was identified (to within a phase) in §4.3.6 as being C_L . The effects of this operator on the annihilation and creation operators of second quantization and on arbitrary shell terms of good quasispin eigenvalues QM_Q are given in equations (4.198), (4.199) and (B.33) respectively. Also since for a shell state transforming as the irreducible representation $\lambda(G)$ (of group G) of dimension λ the value of the quasispin projection eigenvalue is

$$M_Q = \frac{1}{2}(\lambda - N), \quad (4.238)$$

then for a half-filled shell $N = \lambda$ and $M_Q = 0$. So for those terms for which Q , M_Q are applicable eigenvalues (see, for example, §4.3.2 or §4.1.7), for a half-filled shell, $|Q0\rangle$, C_L has eigenvalue $\pi_Q = (-1)^Q$, i.e.

$$C_L|Q0\rangle = \pi_Q|Q0\rangle = (-1)^Q|Q0\rangle. \quad (4.239)$$

Hence in his 1984 paper, when Ceulemans referred to the parity of a half-filled shell state with respect to a linear particle-hole conjugation operator he was actually referring to the “quasispin character” of the state, see equation (4.239). For a half-filled shell state Q is always integral, hence $(-1)^Q = \pi_Q = \pm 1$. This is just the result derived by Ceulemans in 1984 with no knowledge whatsoever of the concept of quasispin. The governing equation from which Ceulemans' 1984 selection rules stem (equation (4.227)), expressed in terms of half-filled shell states, may be labelled with the quasispin scheme proposed by Ceulemans in 1994;

$$\pi_Q \tau_{\mathcal{H}K} \pi_{Q'} \langle Q'0 | \mathcal{H}_k^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_k^K \rangle - \langle Q'0 | \mathcal{H}_k^K | Q0 \rangle, \quad (4.240)$$

where the spin and spatial labels have been suppressed for convenience and the labels K and k now refer to the quasispin rank and projection of the interaction operator ($k = 0$ for a single-

¹⁵In fact the comment in Ceulemans' 1994 paper was that “the relationship between both formalisms is still under study”, with a reference to the communique that inspired this thesis

particle operator, see §4.3.2).

Furthermore the two equations, (4.236) and (4.237), in which Ceulemans 1994 expressed the relationship between the quasispin rank of a single-particle interaction operator and its time-reversal signature, may be summarized

$$\tau_{\mathcal{H}^K} = -(-1)^K, \quad (K = 0, 1). \quad (4.241)$$

With the relationship expressed in this form, and with the knowledge that the C_L parity, π_X , of a state or operator with quasispin rank X and quasispin projection¹⁶ $x = 0$ is

$$\pi_X = (-1)^X; \quad (4.242)$$

then, the relationship between the time-reversal parity, the C_L parity and the quasispin character of a state or operator becomes

$$\tau_{\mathcal{H}^K} = -(-1)^K = -\pi_K. \quad (4.243)$$

In particular equation (4.240) may now be expressed as

$$-\pi_Q \pi_K \pi_{Q'} \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_0^K \rangle - \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle, \quad (4.244)$$

or, in another variation, as

$$-(-1)^{Q+K+Q'} \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_0^K \rangle - \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle. \quad (4.245)$$

Thus two important points have been recovered from a re-expression of Ceulemans 1984 paper:

1. The general rule for the non-vanishing of interaction matrix elements is equivalent to Wybourne's 1991 "crucial" condition on the matrix elements of an interaction between half-filled shells (given here as equation (4.232)), i.e.

$$Q + K + Q' \text{ is even.} \quad (4.246)$$

2. Ceulemans' rules (both versions 1984 and 1994) may be reinterpreted as a general statement about C_L parities: must have

$$\pi_Q \pi_K \pi_{Q'} = +1 \quad (4.247)$$

for the interaction matrix element not to vanish.

¹⁶For example, for a half-filled shell state or a single-particle interaction

Chapter 5

Other Symmetries: Parabose Supersymmetry in Jahn–Teller Systems

Of a slightly more esoteric nature is the matter of parabosons, and of supersymmetry, in Jahn–Teller systems. Schmutz [52] showed in quite some detail, that the $E \otimes e$ Jahn–Teller system can be formulated as a displaced parabose oscillator. Whilst in 1984 Jarvis and Stedman [28] constructed a supersymmetric Hamiltonian for the $E \otimes e$ Jahn–Teller system.

In this chapter it is shown how to incorporate the parabosonic operators of Schmutz into the supersymmetric scheme of Jarvis *et. al.* The result is an elegant representation of the Hamiltonian which manifestly exhibits the symmetry between the plus and minus parabosons.

This chapter was published in 1994 as “Parabosons versus supersymmetry in Jahn–Teller Systems” by Savage & Stedman [51].

5.1 Introduction

Jahn-Teller systems are interesting candidates for nonrelativistic applications of supersymmetry in quantum mechanics because of the degeneracy of the fermion states, the existing fermion-boson interactions and the well-established tradition for applying higher group symmetries to reveal approximate underlying symmetries (for example Pooler and O'Brien [41], Judd [31], Stedman [53]).

The work of Schmutz [52] on parabosons and that of Jarvis *et al.* [28] on supersymmetry, respectively, in $E \otimes \epsilon$ Jahn-Teller Hamiltonians have superficially common features. We show that although the differences in these approaches are fundamental, and do not allow the identification of a parasupersymmetric Jahn-Teller system at this stage, the anharmonic terms introduced by Jarvis *et al.* to achieve supersymmetry may be given elegant representation using paraboson operators.

We take the Hamiltonian to be $H \equiv H_l + H_e + H_c + H_a$ where H_e, H_l are the unperturbed Hamiltonians of the N -fold degenerate electronic system and of a harmonic oscillator with the same degeneracy (so that supersymmetry is possible), H_c is the fermion-boson coupling term and H_a represents anharmonic phonon coupling. In the schemes of Jarvis *et al.* [28] it is vital that anharmonic (boson-boson) couplings in H_c be present to act as the supersymmetric counterparts of the fermion-boson couplings under fermion-boson transmutations. Since physical systems will certainly possess some anharmonicity, this supersymmetric model is expected to be at least as realistic as those assuming harmonic couplings when discussing higher symmetry in Jahn-Teller systems.

In the $E \otimes \epsilon$ system a doubly degenerate vibrational mode (of symmetry ϵ in say the group O) is vibronically coupled to a twofold degenerate (E) electronic level ($H_e = 1$). The fermion-boson coupling has the form $H_c \equiv \sigma_z \phi_1 + \sigma_x \phi_2$ where $\phi_i = b_i + b_i^\dagger$, b_i, f_i are annihilation operators for boson mode and fermion state i , respectively, and σ_z, σ_x are the usual Pauli matrices. We shall write \mathbf{b}, \mathbf{f} for the associated column matrices $(b_i), (f_i)$.

5.2 Supersymmetry in Jahn-Teller systems

We now review and adapt the results of the Jarvis *et al.* formalism. The generator of supersymmetric transformations is the supercharge $S \equiv \mathbf{f}^\dagger \cdot \boldsymbol{\beta}$, where $\boldsymbol{\beta} \equiv \exp G(\boldsymbol{\phi}) \mathbf{b} \exp(-G(\boldsymbol{\phi}))$, $\boldsymbol{\phi} \equiv \{\phi_i\}$, $i = 1, 2$, and G is any real differentiable function of $\boldsymbol{\phi}$. Therefore:

$$[\overleftarrow{\boldsymbol{\beta}}, \overrightarrow{\boldsymbol{\beta}}] = 0, \quad [\overleftarrow{\boldsymbol{\beta}}, \overrightarrow{\mathbf{f}}] = [\overleftarrow{\boldsymbol{\beta}}, \overrightarrow{\mathbf{f}}] = 0,$$

where the left and right arrows indicate row and column labels, respectively. S is nilpotent, and the Hamiltonian $H = \{S, S^\dagger\}$ is necessarily supersymmetric (Witten [63], Blockley *et al.* [5], Stedman [55]).

We may expand $\boldsymbol{\beta}$ in terms of repeated commutators and use the result: $[G(\boldsymbol{\phi}), b_i^{(\pm)}] = \pm G^{(i)}(\boldsymbol{\phi})$, where the superscript i denotes a partial derivative with respect to ϕ_i . Since any two functions of $\boldsymbol{\phi}$ commute we have $\boldsymbol{\beta} = \mathbf{b} - \mathbf{G}'(\boldsymbol{\phi})$. It follows that

$$[\overleftarrow{\boldsymbol{\beta}}, \overrightarrow{\boldsymbol{\beta}^\dagger}] = 1 - 2\mathbf{G}''(\boldsymbol{\phi}).$$

The Hamiltonian becomes

$$\begin{aligned} H &= \mathbf{f}^\dagger [\overleftarrow{\boldsymbol{\beta}}, \overrightarrow{\boldsymbol{\beta}^\dagger}] \mathbf{f} + \boldsymbol{\beta}^\dagger \boldsymbol{\beta}, \\ &= \mathbf{f}^\dagger \mathbf{f} + \mathbf{b}^\dagger \mathbf{b} - 2\mathbf{f}^\dagger \mathbf{G}''(\boldsymbol{\phi}) \mathbf{f} - \mathbf{G}'(\boldsymbol{\phi}) \mathbf{b} - \mathbf{b}^\dagger \mathbf{G}'(\boldsymbol{\phi}) + \mathbf{G}'(\boldsymbol{\phi})^2. \end{aligned} \quad (5.1)$$

This may be written as $H = H_e + H_l + H_c + H_a$, where $H_c = -2\mathbf{f}^\dagger \mathbf{G}''(\boldsymbol{\phi}) \mathbf{f}$ and

$$\begin{aligned} H_a &= -\mathbf{G}'(\boldsymbol{\phi}) \mathbf{b} - \mathbf{b}^\dagger \mathbf{G}'(\boldsymbol{\phi}) + \mathbf{G}'(\boldsymbol{\phi})^2, \\ &= \text{tr} \mathbf{G}''(\boldsymbol{\phi}) - (\mathbf{G}'(\boldsymbol{\phi}))^T \boldsymbol{\phi} + \mathbf{G}'(\boldsymbol{\phi})^2. \end{aligned} \quad (5.2)$$

Jarvis *et al.* point out that each such term in H is guaranteed to be invariant under the point group if the fermions and bosons transform in the same manner and if $G(\boldsymbol{\phi})$ is an invariant function; this follows since $\boldsymbol{\beta} \sim \mathbf{b} \sim \mathbf{f}$ and a contraction such as $\mathbf{f}^\dagger \boldsymbol{\beta}$ is then invariant under the point group.

For the $E \otimes e$ Jahn-Teller system, Jarvis *et al.* [28] choose a $D_4 \supset D_2$ subgroup basis so

that $\phi = (\phi_1, \phi_2)^T \sim ((3z^2 - r^2)/\sqrt{3}, x^2 - y^2)^T$. The only quadratic, cubic and quartic invariants that can be constructed from ϕ are $I_2 \equiv (\phi_1^2 + \phi_2^2)$, $I_3 \equiv (\phi_1^3 - 3\phi_1\phi_2^2)$, and $I_4 \equiv I_2^2$. Also $\Phi \equiv (\phi_1^2 - \phi_2^2, -2\phi_1\phi_2)^T$ transforms as ϕ . If $G_E \equiv -\frac{1}{3}\alpha I_3$, then $\beta = \mathbf{b} + \alpha\Phi$ and

$$\begin{aligned} H_c &= -2\mathbf{f}^\dagger \begin{pmatrix} -2\alpha\phi_1 & 2\alpha\phi_2 \\ 2\alpha\phi_2 & 2\alpha\phi_1 \end{pmatrix} \mathbf{f} \\ &= 4\alpha(\phi_1(f_1^\dagger f_1 - f_2^\dagger f_2) - \phi_2(f_1^\dagger f_2 - f_2^\dagger f_1)) \\ &= 4\alpha\mathbf{f}^\dagger(\phi_1\sigma_z - \phi_2\sigma_x)\mathbf{f}. \end{aligned} \quad (5.3)$$

G_E generates a mixture of cubic and quartic anharmonicity: $H_a = \alpha I_3 + \alpha^2 I_4$. Thus,

$$H_{JS} = H_2 + H_e + H_c + H_a = \mathbf{b}^\dagger \mathbf{b} + \mathbf{f}^\dagger \mathbf{f} + 4\alpha\mathbf{f}^\dagger(\phi_1\sigma_z - \phi_2\sigma_x)\mathbf{f} + \alpha I_3 + \alpha^2 I_4. \quad (5.4)$$

On projecting out the fermion operators $H_{JS} \rightarrow \mathbf{H}_{JS}$ by the relation $H_{JS} \equiv \mathbf{f}^\dagger \mathbf{H}_{JS} \mathbf{f}$, we find

$$\begin{aligned} \mathbf{H}_{JS} &= [\overleftarrow{\beta}, \overrightarrow{\beta}^\dagger] + (\beta^\dagger \beta) \mathbf{1}, \\ &= (\mathbf{b}^\dagger \mathbf{b} + 1 + \alpha I_3 + \alpha^2 I_4) \mathbf{1} + 4\alpha(\phi_1\sigma_z - \phi_2\sigma_x). \end{aligned} \quad (5.5)$$

5.3 Parabosons in Jahn-Teller systems

Similarly, we briefly review and adapt the representation by Schmutz [52] of an $E \otimes \epsilon$ Jahn-Teller system in terms of displaced parabose oscillators (we use $\alpha = \lambda/4$, $\phi_2 \rightarrow -\phi_2$). Schmutz begins with the $E \otimes \epsilon$ Jahn-Teller Hamiltonian $\mathbf{H}_2 + \mathbf{H}_e + \mathbf{H}_c$:

$$\mathbf{H}_S = (\mathbf{b}^\dagger \mathbf{b} + 1) \mathbf{1} + 4\alpha(\phi_1\sigma_z - \phi_2\sigma_x) = (\mathbf{b}^\dagger \mathbf{b}) \mathbf{1} + [\overleftarrow{\beta}, \overrightarrow{\beta}^\dagger]. \quad (5.6)$$

Note the omission of anharmonicity. The operator $\Gamma_i \equiv \exp(i\pi b_i^\dagger b_i)$ and has the useful properties $\Gamma_i^\dagger = \Gamma_i^{-1}$, $\{\Gamma_i, b_i\} = 0$, $\Gamma_i |n_i\rangle = (-1)^{n_i} |n_i\rangle$; in addition, since Γ_i^2 has expectation value unity in any space of definite (integer) number, and commutes with all operators in the theory, we can take $\Gamma_i = \Gamma_i^\dagger = \Gamma_i^{-1}$ in all relations. A derived unitary operator \mathbf{U}_1 diagonalizes \mathbf{H}_S :

$$\mathbf{U}_i = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & \Gamma_i \\ 1 & -\Gamma_i \end{pmatrix}, \quad \mathbf{H}_S' = \mathbf{U}_1 \mathbf{H}_S \mathbf{U}_1^\dagger = \begin{pmatrix} H_- & 0 \\ 0 & H_+ \end{pmatrix}; \quad (5.7)$$

$$H_\eta \equiv \mathbf{b}^\dagger \mathbf{b} + 1 + 4\alpha(\phi_1 + \eta\phi_2\Gamma_1), \quad (5.8)$$

where $\eta = \pm$. The operators a_i, a_i^\dagger where $a_i \equiv b_i \Gamma_{3-i}$, $i = 1, 2$, obey boson commutation relations amongst themselves (as do b_i, b_i^\dagger), but each has zero anticommutator with each of b_i, b_i^\dagger . $\mathbf{A} \equiv (A_+, A_-)^T = \mathbf{U}_1 \mathbf{b}$, $A_\eta \equiv (b_1 + \eta a_2)/\sqrt{2}$. These operators satisfy the trilinear commutation relations characteristic of all $p = 2$ parabosonic operators (where ζ , like η , is either $+$ or $-$) (see for related material Green [21], Greenberg and Messiah [22], Rubakov and Spironodov [48], Beckers and Debergh [2, 3], Bardakci [1]:

$$[\{A_\eta, A_\eta^\dagger\}, A_{-\eta}] = -A_{-\eta}, [\{A_\eta, A_\eta\}, A_\eta^\dagger] = 2A_\eta, [\{A_\eta, A_\eta\}, A_\zeta] = 0. \quad (5.9)$$

Other such relations follow by hermitian conjugation and also by the generalized Jacobi identity. A_\pm may be defined by the relations $[N_\zeta, A_\eta] = -A_\eta$, where $N_\zeta \equiv \{A_\zeta, A_\zeta^\dagger\}$. In the two-dimensional case, $N_+ = N_- \equiv N$ and is the number operator for the system. The unperturbed Hamiltonian of the two dimensional harmonic oscillator, $H_2 = \mathbf{b}^\dagger \mathbf{b} + 1$, may be written as $H_2 = N = \mathbf{A}^\dagger \mathbf{A} + 1$. H_η can therefore be expressed as $H_\eta = N'_\eta - 16\alpha^2$, where $N'_\zeta \equiv \{A'_\zeta, A'^\dagger_\zeta\}$ and $A'_\eta \equiv A_\eta + 2\sqrt{2}\alpha$ so that $N'_\zeta = N + 2\sqrt{2}\alpha (A_\zeta + A^\dagger_\zeta) + 8\alpha^2$.

Hence the Hamiltonians H_η are identical with those of displaced parabose oscillators (A_η being the parabose operator and $2\sqrt{2}\alpha$ its displacement). Under the unitary transformation \mathbf{U}_1 in which $\mathbf{H}_S \rightarrow \mathbf{H}'_S$, $\mathbf{f} \rightarrow \mathbf{f}'$ (which preserves the Fermi anticommutation relations), then $H_S = \mathbf{f}'^\dagger \mathbf{H}'_S \mathbf{f}'$, and parabosonic expressions are obtained in the Hamiltonian. The Schmutz diagonalisation process may thus be viewed as a result of this unitary symmetry of the formalism.

5.4 Action of Schmutz transformations in the Jarvis et al. hamiltonian

An obvious question is: what is the action of the Schmutz unitary diagonalising matrix \mathbf{U}_1 on the Jarvis *et al.* Hamiltonian \mathbf{H}_{JS} ? Let $\mathbf{H}_{JS} \rightarrow \mathbf{H}'_{JS}$, $\mathbf{f} \rightarrow \mathbf{f}'$ and $\beta \rightarrow \beta'$ under \mathbf{U}_1 . We obtain $\mathbf{H}'_{JS} = \mathbf{H}'_S + \alpha I_3 \sigma_x + \alpha^2 I_4 \mathbf{1}$. Since $H_{JS} = \mathbf{f}'^\dagger \mathbf{H}'_{JS} \mathbf{f}'$, this may be regarded as the original Hamiltonian in a unitarily transformed fermion basis. We note also that $S = \mathbf{f}'^\dagger \beta'$, where

$\beta' \equiv \mathbf{A} + \alpha \mathbf{P}_1$ and

$$\mathbf{P}_1 \equiv \sqrt{2} \begin{pmatrix} C_- C_+ \\ C_+ C_- \end{pmatrix}$$

with $C_\zeta \equiv A_\zeta + A_\zeta^\dagger$. Hence S also involves paraboson operators, and the (supersymmetric) Hamiltonian

$$H_{JS} = (\mathbf{f}'^\dagger \beta') (\beta'^\dagger \mathbf{f}') + (\beta'^\dagger \mathbf{f}') (\mathbf{f}'^\dagger \beta') = \mathbf{f}'^\dagger \mathbf{H}'_{JS} \mathbf{f}'.$$

Since $\mathbf{b}^\dagger \mathbf{b} = \mathbf{A}^\dagger \mathbf{A}$,

$$\beta'^\dagger \beta' = \mathbf{A}^\dagger \mathbf{A} + \alpha(\mathbf{A}^\dagger \mathbf{P}_1 + \mathbf{P}_1^\dagger \mathbf{A}) + \alpha^2 \mathbf{P}_1^\dagger \mathbf{P}_1, \quad (5.10)$$

$I_3 = \sqrt{2}(\mathbf{A}^\dagger \mathbf{P}_1 + \mathbf{P}_1^\dagger \mathbf{A}) = C_+ C_- C_+$, $I_4 = \mathbf{P}_1^\dagger \mathbf{P}_1 = \{C_+ C_-, C_- C_+\}$, and so the Jahn-Teller Hamiltonian may be written

$$H_{JS} = \mathbf{f}'^\dagger \left(\mathbf{H}_S + \alpha(\mathbf{P}_1^\dagger \mathbf{A} + \mathbf{A}^\dagger \mathbf{P}_1) \sigma_x + \alpha^2 \mathbf{P}_1^\dagger \mathbf{P}_1 \right) \mathbf{f}'. \quad (5.11)$$

At this point we simply follow Schmutz's method for rendering such a Hamiltonian diagonal, using the fermion transformation associated with \mathbf{U}_2 ; and, as in the work of Schmutz, the effect is to highlight further the paraboson operators. If $\mathbf{U} \equiv \mathbf{U}_2 \mathbf{U}_1$, $\mathbf{H}_{JS} \rightarrow \mathbf{H}''_{JS}$, $\mathbf{f} \rightarrow \mathbf{f}''$ and $\beta \rightarrow \beta''$ under \mathbf{U} then:

$$\mathbf{H}''_{JS} = (\mathbf{b}^\dagger \mathbf{b} + 1 + 4\alpha(\phi_1 - \phi_2 \Gamma_1)) \mathbf{1} + \alpha I_3 \Gamma_2 \sigma_z + \alpha^2 I_4 \mathbf{1} = \begin{pmatrix} H_{JS+} & 0 \\ 0 & H_{JS-} \end{pmatrix}, \quad (5.12)$$

where

$$\begin{aligned} H_{JS\eta} &= \mathbf{b}^\dagger \mathbf{b} + 1 + 4\alpha(\phi_1 - \phi_2 \Gamma_1) + \eta \alpha I_3 \Gamma_2 + \alpha^2 I_4 \\ &= (N'_- - 16\alpha^2 + \alpha^2 I_4) \mathbf{1} + \eta \alpha I_3 \Gamma_2 \end{aligned} \quad (5.13)$$

or, in terms of paraboson operators:

$$\mathbf{H}_{JS} = (N'_- - 16\alpha^2) \mathbf{1} + \alpha(\mathbf{P}_1^\dagger \mathbf{A} + \mathbf{A}^\dagger \mathbf{P}_1) \Gamma_2 \sigma_z + \alpha^2 (\mathbf{P}_1^\dagger \mathbf{P}_1) \mathbf{1}.$$

Hence

$$H_{JS} = \mathbf{f}''^\dagger (\mathbf{U} [\overleftarrow{\beta}, \overrightarrow{\beta}^\dagger] \mathbf{U}^\dagger + \mathbf{U} \beta''^\dagger \beta'' \mathbf{U}^\dagger) \mathbf{f}''. \quad (5.14)$$

It is instructive to write in the last term

$$\beta''^\dagger \beta'' = \beta^\dagger (\Gamma_2 \mathbf{U}_2)^\dagger (\Gamma_2 \mathbf{U}_2) \beta = \mathbf{b}^\dagger \mathbf{b} + \alpha (\mathbf{B}^\dagger \mathbf{P}_2 + \mathbf{P}_2^\dagger \mathbf{B}) \Gamma_2 + \alpha^2 \mathbf{P}_2^\dagger \mathbf{P}_2, \quad (5.15)$$

where

$$\mathbf{B} \equiv \begin{pmatrix} B_+ \\ B_- \end{pmatrix} = \Gamma_2 \mathbf{U}_2 \mathbf{b}, \quad \mathbf{P}_2 \equiv \mathbf{U}_2 \Phi = \sqrt{2} \begin{pmatrix} D_+ D_- \\ D_- D_+ \end{pmatrix},$$

$$D_\zeta \equiv B_\zeta + B_\zeta^\dagger, \quad B_\zeta \equiv (b_1 \Gamma_2 + \zeta b_2) / \sqrt{2}.$$

$\{B_\zeta\}$ are therefore para-boson operators (i.e. obey a mixture of commutation and anti-commutation relations). In addition $\mathbf{B}^\dagger \mathbf{B} = \mathbf{b}^\dagger \mathbf{b} = \mathbf{A}^\dagger \mathbf{A}$, $I_3 = (\mathbf{B}^\dagger \mathbf{P}_2 + \mathbf{P}_2^\dagger \mathbf{B}) \Gamma_2$, $I_3 \Gamma_2 = \sqrt{2} (D_+ D_- D_+ + D_- D_+ D_-)$, $I_4 = \mathbf{P}_2^\dagger \mathbf{P}_2 = 2 \{D_+ D_-, D_- D_+\}$, so that

$$\mathbf{U} \beta^\dagger \beta \mathbf{U}^\dagger = \mathbf{A}^\dagger \mathbf{A} + \alpha (\mathbf{B}^\dagger \mathbf{P}_2 + \mathbf{P}_2^\dagger \mathbf{B}) \Gamma_2 + \alpha^2 \mathbf{P}_2^\dagger \mathbf{P}_2, \quad (5.16)$$

and thus

$$\mathbf{H}_{JS}(\mathbf{A}, \mathbf{B}) = (N'_- - 16\alpha^2) \mathbf{1} + \alpha (\mathbf{P}_2^\dagger \mathbf{B} + \mathbf{B}^\dagger \mathbf{P}_2) \sigma_z + \alpha^2 (\mathbf{P}_2^\dagger \mathbf{P}_2) \mathbf{1}. \quad (5.17)$$

This is a diagonal Hamiltonian expressed entirely in terms of parabosons.

Remarkably the anharmonic terms are very amenable to expression in terms of paraboson operators. The cubic and quartic anharmonicity invariants I_3 and I_4 have in fact a far more elegant relationship when so expressed; the symmetry between the plus and minus parabosons is manifest.

5.5 Parasupersymmetry?

All of the former analysis is confined to standard fermi-bose supersymmetry, whose generator and spectrum are those reported in Jarvis *et al.* [28]. However the above analysis is suggestive of a role for parasupersymmetry in Jahn-Teller theory.

The usual approach, however, is to use parafermi-bose supersymmetry (Jarvis [27], Rubakov *et al.* [48], Beckers and Debergh [2]). This can lead to spectra with threefold degeneracies. Such

a possibility of alternative higher symmetries would continue and enhance the above-mentioned tradition for applying higher group symmetries in Jahn-Teller systems.

Following the first example of Rubakov *et al.*, we might search for parasupersymmetry using the paracharge

$$Q = \begin{pmatrix} 0 & 0 & 0 \\ p + iW_1 & 0 & 0 \\ 0 & p + iW_2 & 0 \end{pmatrix},$$

leading to a Hamiltonian of the form

$$H = \frac{1}{2}p^2 + W_1^2 + W_2^2 + \frac{1}{3}(W_1' - W_2') + \frac{1}{3} \begin{pmatrix} 2W_1' + W_2' & 0 & 0 \\ 0 & W_2' - W_1' & 0 \\ 0 & 0 & -W_1' - 2W_2' \end{pmatrix}$$

For this to replicate, say the $T \times \epsilon$ Jahn-Teller system, we need to identify this interaction by an appropriate choice of the superpotentials W_1, W_2 . The $T \times \epsilon$ Jahn-Teller system has an interaction, when diagonalised, of the form:

$$\begin{pmatrix} \sqrt{\phi_1^2 + \phi_2^2} & 0 & 0 \\ 0 & -\sqrt{\phi_1^2 + \phi_2^2} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Hence we would have to identify

$$2W_1' + W_2' = W_1' - W_2' = 3W_1'/2 = \sqrt{\phi_1^2 + \phi_2^2}, \quad W_1' = -2W_2'.$$

While these relations are algebraically consistent, each potential must contain both ϕ_1 and ϕ_2 ; in addition, the further conditions required by Rubakov *et al.* give the unlikely requirement that $W_2'(W_2 + 2W_1) = 3W_2''$. This approach therefore seems unpromising. Nevertheless the paraboson link established here may help to indicate a better direction for studying possible realisations of parasupersymmetric systems.

Chapter 6

Conclusion

The primary aim of the proposal that inspired this thesis was to uncover the relationships between several disparate approaches to the common problem of describing, in general terms, the effects of particle-hole conjugation in instances of reduced symmetry. This aim has been achieved, and the relationships amongst the differing methodologies made transparent.

Two burning questions at the initiation of this investigation were how it was that Ceulemans [12, 13]:

1. Achieved sets of selection rules for half-filled shells that were apparently not reproduced elsewhere in the literature.
2. Derived these selection rules twice, by dramatically different methods, and yet, according to Ceulemans himself [13] was unable to resolve the formalisms.

In answer to (1), it is now clear that the extra step that Ceulemans took in both instances was the inclusion of time reversal in the formalism. Although Bell [4] had determined the effect of a linear particle-hole conjugation operator on shell states, and had managed to derive a relationship between matrix elements of conjugate states, he did not examine the effects of time reversal on these shell states in conjunction with the operation of a linear particle-hole conjugation.

Wybourne in 1973 for ligand fields and in 1991 for atomic d^n and f^n configurations arrived

at theorems for half-filled shells, in both instances involving the quasispin concept. It fell to Ceulemans in 1994 however, to determine the relationship between the quasispin rank of an operator, and its behaviour under time reversal. Thus leading to selection rules for matrix elements of a single-particle interaction between half-filled shell states. The step that Ceulemans appears to not have been aware of, however, was to present the quasispin rank — time-reversal parity relationship in the form:

$$\tau_{\mathcal{H}Q} = -(-1)^Q. \quad (6.1)$$

Once the expression is written in this manner and with the knowledge that a state or operator scalar in quasispin (as for a half-filled shell or a single-particle interaction) has parity π_Q with respect to the linear particle-hole conjugation operator C_L of the form

$$\pi_Q = (-1)^Q, \quad (6.2)$$

then the relationship between the Ceulemans' selection rules of 1984 (Selection Rules 4.3.1), which were phrased in terms of the parity of states with respect to a linear particle-hole conjugation operator and the time reversal nature of the interaction, and the Ceulemans' selection rules of 1994 (Selection Rules 4.3.2), which were phrased in terms of the “quasispin character” of the states and the time reversal nature of the interaction, is surprisingly straightforward.

In the process of arriving at the connection between the two Ceulemans papers, described above, the methodology used by Ceulemans in 1984 to derive the rules themselves was generalized by the process of second quantization and by making as few assumptions as possible about the symmetry properties of the relevant groups. This generalization process is encapsulated in the notation used to express the equations. A full description of the assumptions made, and the notation used in this generalization process is contained in Appendix A.

A very important technique of checking the veracity of these generalized equations is an adaptation of the diagram techniques of “good housekeeping” as outlined in Stedman’s 1990 book on the subject of diagram techniques in group theory (Stedman [57]). The conditions of maintaining a “bipartite” diagram is transliterated into a similar condition for second quantised algebraic

equations. Chapter 2 is devoted to this technique.

It is discovered in §4.2.2.6 that some of Stedman's equations (definitions and proofs) fail to meet the requirements of biparticity. They are modified so that they do. Consequently some of the properties of C_A (C_A is the notation used in this thesis to refer to Stedman's 1987, antilinear particle-hole conjugation operator) as given in Stedman [56] are not correct without the restriction that the $2jms$ be chosen real. According to the discussion and tables contained in Butler [9], it would appear to always be possible to make the choice of reality of the $2jms$ for all point groups. However Butler [9] refers the reader to his 1975 paper (Butler [8]) in which this choice of reality is merely hypothesised. The arguments contained in Stedman [56] then, while perhaps not being incorrect as such, certainly do appear to lose some of their generality.

The importance of whether or not the $2jms$ in Stedman [56] are real is, of course, related to the fact that Stedman defines an antilinear particle-hole conjugation operator C_A . This definition is given by the relationship

$$C_A \equiv C_L Z, \tag{6.3}$$

where C_L is the well defined linear particle-hole conjugation operator used, for example, by Bell [4] and given an explicit definition in terms of second-quantized operators by Keiter et al [34]. The Z factor denotes the operator corresponding to complex conjugation.

The inclusion of Z in this manner, causes one other problem in the list of properties of C_A , given in Stedman [56], which can not be overcome by choosing the $2jms$ to be real. Property (d), that C_A commutes with ordinary spin, is found to be in error, since the y component of spin is, in fact, complex.

Through the process of modifying the definition of C_A , in order that its properties be consistent with the requirements of biparticity, it was discovered that the modified operator, denoted C'_A ,

was in fact equivalent to the composite operator $C_L T$. That is

$$C'_A \equiv C_L T. \quad (6.4)$$

Why this should be so follows from the fact that the technique of modifying equations so they are bipartite, involves the judicious addition of $2jm$ symbols (see Chapter 2 of this thesis or Stedman's Book [57]). These symbols are elements of the unitary matrix included by Wigner in his definition of time reversal T . This matrix is denoted \mathcal{J} in this thesis, i.e.

$$T \equiv \mathcal{J} Z. \quad (6.5)$$

The truly remarkable consequence of the requirement of biparticity and hence the definition of C'_A is that in §4.3.3 C'_A is found to be equivalent to the antilinear particle-hole conjugation operator $O(\varphi)$, from which Ceulemans' 1984 selection rules stem.

A chart depicting the relationship between the major operators referred to in this thesis, is to be found in Figure 6.1.

Included in this thesis (appearing as Chapter 5) is a paper published in 1994 [51] which is written in conjunction with Professor Stedman. The paper discussed an attempt to merge the concepts of parabose statistics and supersymmetry with respect to the $E \times e$ Jahn-Teller system. It was concluded that it was indeed possible to introduce the parabose operators of Schmutz [52] into the supersymmetric Hamiltonian of Jarvis & Stedman [28].

6.1 Scope for further work

The theoretical aspects of this thesis are fascinating to the author. The fact that symmetries other than the obvious spatial symmetries of systems should have such a profound effect on the allowable interaction matrix elements is quite remarkable.

However the theoretical aspects of this work are obviously tempered by the need for experimental verification. Ceulemans [11, 15] has already proposed his selection rules as possible

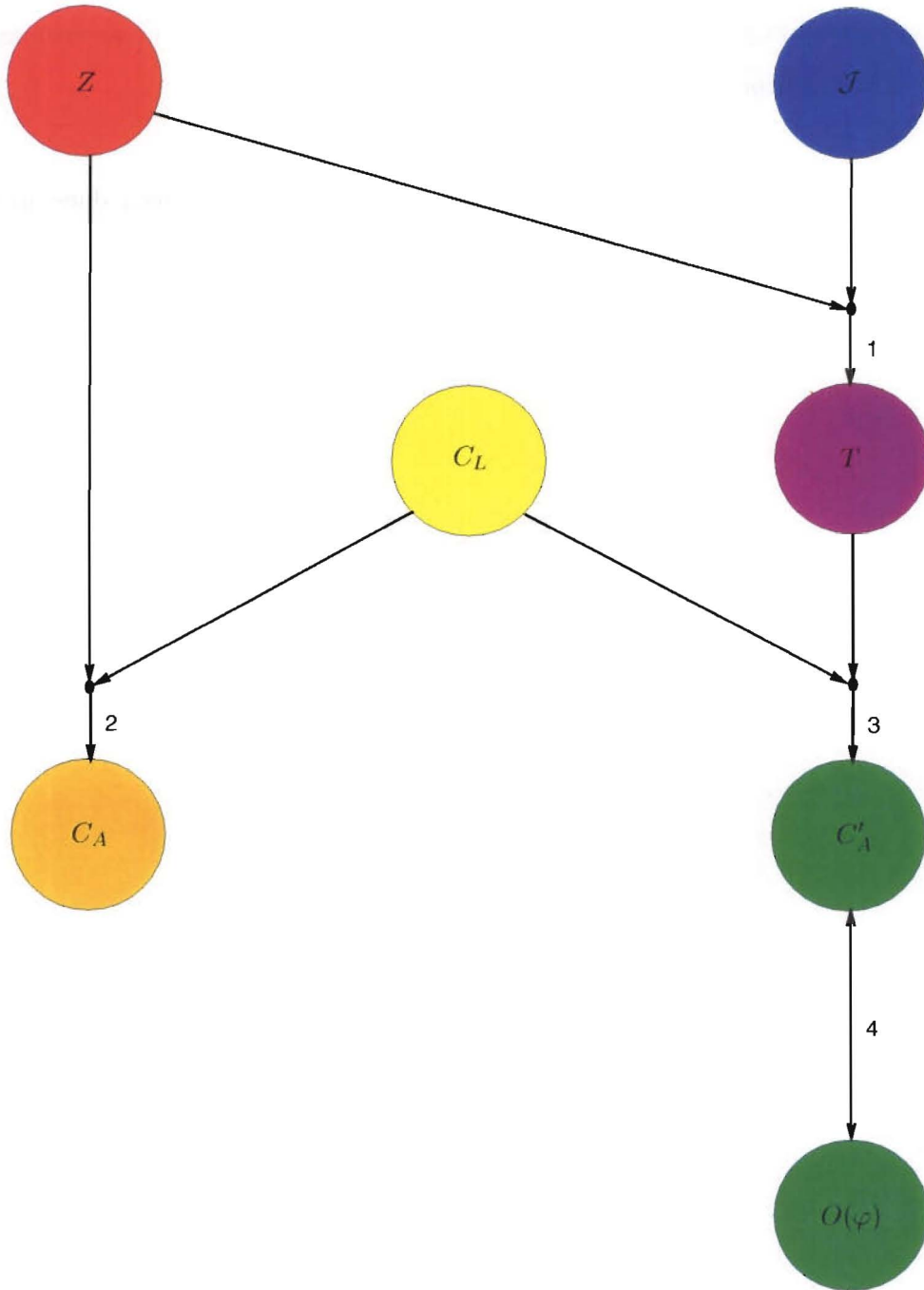


Figure 6.1: The relationship between the main operators discussed in this thesis. Relation (1) is Wigner's definition of T , relation (2) is from Stedman [56], relation (3) is by the definition in §4.2.2.6 and equivalence (4) is reached in §4.3.4, where $O(\varphi)$ is Ceulemans' antilinear operator.

explanation for several phenomena reported in the literature. However more work needs to be done in correlating theory with experiment.

In addition, it is regretted by the author that more work has not been done to push still further the results of Chapter 5. As mentioned there, the great variety of Jahn-Teller systems, in particular $T \times t$ ones, should be amenable to be expressed in these formalisms.

Appendix A

$2jm$ and $3jm$ symbols

A.1 State labelling scheme

The labelling of states in this thesis is based on the conventions used in Stedman's "Diagram Techniques in Group Theory" [57], which in turn is based on Butler's scheme in his 1981 book "Point Group Symmetry Applications: Methods and Tables" [9].

A three stage labelling scheme is used for an N particle eigenstate $|K\rangle \equiv |K\kappa k\rangle$, where the labels $K = J^\pi, \kappa, k$ are irreducible representations of $O(3)$, of the appropriate subgroup G and of its subgroup H . These three groups are found to suffice for labelling and occasionally just two will be adequate, in which case the unnecessary irreducible representation label will be suppressed (as in the instance of $|jm\rangle$ for the $SO(3) \supset SU^S(2)$ chain). Therefore in a second quantized expression a_{Kk}^\dagger or $a_{K\kappa}^\dagger$ may be seen.

The group G could possibly be either a product spin/space group, i.e. $G = G \times SU^S(2)^N$ (in which case the higher group would have to be $O(3) \times SU^S(2)^N$) or, as is assumed in this thesis, the coupled group in which the total angular momentum $\underline{J} = \underline{L} + \underline{S}$ provides the basis of the labelling scheme and projective representations are included.

For each state $|K\rangle$ the great orthogonality theorem (more specifically the character orthogo-

nality theorem — see Stedman [57] for a diagram proof of this) proves that there exists one so call conjugate state $|\bar{K}\rangle$ such that the direct product of the irreducible representations corresponding to the labels K and \bar{K} is identically equal to the group invariant. For example for the full rotation group, G may be taken to be the product space/spin group $O(3) \times SU^S(2)$ and the state may be labelled $K, k = j, m$ with the conjugate state labelled $\bar{K}, \bar{k} = j, -m$.

A.2 Properties of the $2jm$ symbols

The $2jm$ symbols, (KL) , are elements of a unitary matrix which shall be denoted \mathcal{J} , where the notation used in this thesis to denote the $2jm$ symbol is that used by Stedman [56]. The matrix \mathcal{J} is that corresponding to Wigner's C (see Wigner [62]) which complex conjugates the matrices of the irreducible representation λ of the group G , i.e.

$$\mathcal{J}\lambda(R)\mathcal{J}^{-1} = \lambda(R)^*. \quad (\text{A.1})$$

The matrices \mathcal{J} can be shown to be either symmetric or antisymmetric, i.e.

$$\mathcal{J}^T = \{K\}\mathcal{J}, \quad \{K\} = \pm 1. \quad (\text{A.2})$$

Using these properties of \mathcal{J} , restrictions can be placed on its elements — the $2jm$ symbols (KL) .

The rows and columns of the \mathcal{J} matrix for the group G are labelled by the irreducible representation labels K and L respectively (these may very well be composite labels, e.g. $m_s m_l$ or, another possibility, $ja\lambda l$). So that $\mathcal{J}_{KL} \equiv (KL)$, i.e. the KL th element of the matrix \mathcal{J} is the $2jm$ symbol (KL) .

In terms of its components, the unitarity of \mathcal{J} implies:

$$\mathcal{J}_{KL}\mathcal{J}_{LK'}^\dagger = \delta_{KK'} \quad (\text{A.3})$$

$$\text{i.e. } \mathcal{J}_{KL}\mathcal{J}_{K'L}^* = \delta_{KK'} \quad (\text{A.4})$$

$$\Rightarrow (KL)(K'L)^* = \delta_{KK'}. \quad (\text{A.5})$$

Whilst equation (A.2) gives

$$\mathcal{J}_{KL}^T = \{K\} \mathcal{J}_{KL} \quad (\text{A.6})$$

$$\text{i.e. } \mathcal{J}_{LK} = \{K\} \mathcal{J}_{KL}. \quad (\text{A.7})$$

$$\Rightarrow (LK) = \{K\}(KL) \quad (\text{A.8})$$

Substituting equation (A.5) into equation (A.8) leads to

$$(LK)(K'L)^* = \{K\} \delta_{KK'}. \quad (\text{A.9})$$

The $2jm$ symbols are in fact a special case of the $3jm$ symbols. They are Clebsch-Gordon coupling coefficients describing the coupling of two irreducible representations to an invariant of G , which has been renormalized,

$$\begin{pmatrix} \lambda_1 & \lambda_2 \\ l_1 & l_2 \end{pmatrix} = |\lambda_1|^{\frac{1}{2}} \langle 0 | \lambda_1 l_1 \lambda_2 l_2 \rangle. \quad (\text{A.10})$$

Equation (A.10) is in Butler [9].

Some important points to note at this stage are that

1. As the scalar irreducible representation of the group G , $0(G)$, is always of unit dimension it only has the one partner so the partner label (e.g. l_1, l_2) may be omitted without ambiguity.
2. The scalar irreducible representation $0(G)$ (using Butler [9] notation) occurs once and only once in the direct product $\lambda_1(G) \times \lambda_2(G)$ and then if and only if $\lambda_2(G) = \lambda_1^*(G)$.

Denoting the irreducible representation and partner labels λ_1, l_1 and λ_2, l_2 by the composite labels K and L the above may be summarized by

$$\begin{pmatrix} \lambda_1 & \lambda_2 \\ l_1 & l_2 \end{pmatrix} \equiv (KL) \equiv (K\bar{K}), \quad (\text{A.11})$$

where \bar{K} represents the complex conjugate irreducible representation and partner labels.

Butler (Butler [9], Chapter 3) discussed in full detail the properties of the $j\bar{m}$ factors and j symbols. In particular the use of the factorization lemma of Racah, which may be used to greatly simplify $j\bar{m}$ symbols for a group-subgroup chain in terms of products of $j\bar{m}$ factors. For example for the $SO(3) \supset G \supset C_1$ chain with irreducible representations $J(SO3)$, $\lambda(G)$ and $0(C_1)$ the $2j\bar{m}$ symbols is the product of the $2j\bar{m}$ factor for $SO(3) \supset G$ and a $2j\bar{m}$ factor for $G \supset C_1$

$$\begin{pmatrix} J \\ a \\ \lambda \\ b \\ 0 \end{pmatrix}_{C_1}^{SO(3)} = \begin{pmatrix} J \\ a \\ \lambda \end{pmatrix}_G^{SO(3)} \begin{pmatrix} \lambda \\ b \\ 0 \end{pmatrix}_{C_1}^G, \quad (A.12)$$

where a and b are branching multiplicities. For point groups these branching multiplicities are real numbers and this fact enables a simplified single column notation to be used with no loss of information. The dimension factor in equation (A.10) ensures that the non-zero $2j\bar{m}$ factors in an expression such as equation (A.12) are always ± 1 .

Equation (A.11) allows the following simplification for equations (A.5), (A.8) and (A.9)

$$(K\bar{K})(K\bar{K})^* = 1 \quad (A.5')$$

$$(\bar{K}K) = \{K\}(K\bar{K}) \quad (A.8')$$

$$(\bar{K}K)(K\bar{K})^* = \{K\}. \quad (A.9')$$

A.3 Properties of the $3j\bar{m}$ symbols

The $3j\bar{m}$ symbol

$$\begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (A.13)$$

couple the three irreducible representations labelled \bar{K} , M and L to an invariant, or equivalently the two irreducible representations M and L to \bar{K} (or any cyclic permutation there of). The

$3jm$ symbols are just numbers (possibly complex) and are tabulated, see for example Butler [9]. The product multiplicity “ r ” indicates the instance of the occurrence of the product $M \times L$ in \bar{K} . These occurrences are arbitrarily labelled from 0.

Some assumptions are made about (A.13) in this thesis. The group to which the irreducible representations \bar{K} , M and L belong is assumed to be simple phase (as are most point groups). That is the $3jm$ symbol

$$\begin{pmatrix} \bar{K} & L & M \\ \bar{k} & l & m \end{pmatrix}^r, \quad (\text{A.14})$$

which is obtained from (A.13) by a transposition of columns 2 and 3, is equal to (A.13) by a phase — the $3j$ phase $\{\bar{K}MLr\}$, which has values of ± 1 (and are tabulated, for example, in Chapter 14 of Butler [9]). The assumption of simple phase groups ensures that the same phase occurs upon transposition of any two of the three columns. The $3j$ phase has the same value under conjugation of the irreducible representation labels, i.e. $\{\bar{K}MLr\} = \{K\bar{M}\bar{L}r\}$.

Another important assumption about the groups used in this thesis is that they satisfy *quasi-ambivalence*, i.e. the product of the three $2j$ phases of the irreducible representations \bar{K}, L, M appearing in the $3j$ symbol (A.13) is equal to unity

$$\{K\}\{M\}\{L\} = 1. \quad (\text{A.15})$$

This assumption of quasiambivalence has direct consequences when the effect of complex conjugation is considered on the $3jm$ symbols.

The complex conjugated $3jm$ symbol

$$\begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^{*r} \quad (\text{A.16})$$

can be shown to be equal to the product of three $2jm$ symbols and the unconjugated $3jm$ symbol, i.e.

$$\begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^{*r} = (\bar{K}K)(M\bar{M})(L\bar{L}) \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r. \quad (\text{A.17})$$

Quasiambivalence implies that the doubly conjugated $3jm$ symbol returns the unconjugated symbol (since $(\bar{K}K)^*(K\bar{K}) = \{K\}$ and so on).

Last, but certainly not least in importance, is the property that the $3jm$ is invariant under cyclic permutations of its columns.

A.3.1 Spherical symmetry

The relationship between the Clebsch-Gordan coefficients and the $3j$ symbols of $\text{SO}(3)$ is

$$\langle j_1 m_1 j_2 m_2 | JM \rangle = \frac{\sqrt{2J+1}}{(-1)^{j_1-j_2-M}} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}. \quad (\text{A.18})$$

In addition to the general rules for $3jm$ symbols there are some $\text{SO}(3)$ specific rules of paramount importance to the results of this thesis.

1. Reality:

$$\langle j_1 m_1 j_2 m_2 | JM \rangle^* = \langle j_1 m_1 j_2 m_2 | JM \rangle. \quad (\text{A.19})$$

2. Selection Rules: “Triangular Inequalities”

$$\left. \begin{array}{l} m_1 + m_2 = M \\ |j_1 - j_2| \leq j_1 + j_2 \end{array} \right\} \text{ else } \langle j_1 m_1 j_2 m_2 | JM \rangle = 0. \quad (\text{A.20})$$

3. Symmetries: $\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & M \end{pmatrix}$ is

(a) Invariant in a circular permutation of the three columns.

(b) Multiplied by $(-1)^{j_1+j_2+J}$ in a permutation of any two columns.

(c) Multiplied by $(-1)^{j_1+j_2+J}$ under a simultaneous change of signs of m_1 , m_2 and M .

4. Symmetries of the Clebsch-Gordan coefficients follow from the corresponding symmetries of the $3jm$ symbols and the defining relationship A.3.1.

$\langle j_1 m_1 j_2 m_2 | JM \rangle$ is:

- (a) Invariant in a circular permutation of the three columns.
- (b) Multiplied by $(-1)^{j_1+j_2-J}$ in a permutation of any two columns.
- (c) Multiplied by $(-1)^{j_1+j_2-J}$ under a simultaneous change of signs of m_1 , m_2 and M .

Appendix B

Proofs of properties of C_L

B.1 C_L is unitary

C_L is unitary, i.e. $C_L C_L^\dagger = C_L^\dagger C_L = 1$. A few results are required to prove this, where the following proof is for $G(K)$ defined as in equation (4.120) with the proof for equation (4.55) being similar:

(a) $G(K)^\dagger = G(K)$: this is trivial since $G(K) = 2Q(K)_x$ and the cartesian components of quasispin are hermitian.

(b) $F(K)^\dagger = F(K)$; also trivial. From the definition of $F(K)$

$$F(K) = n(K) + n(\bar{K}) - 2n(K)n(\bar{K}) \quad (\text{B.1})$$

and using the results that $n(K)^2 = n(K)$ and $n(\bar{K})^2 = n(\bar{K})$ it follows that

(c) $F(K)^2 = F(K)^\dagger F(K) = F(K)$.

(d) $\{G(K), F(K)\} = 0$: this follows from the definitions of $G(K)$ and $F(K)$ and from equation (D.22) (which may be restated as $Q(K)_x^2 = Q(K)_y^2 = Q(K)_z^2$).

(e) $G(K)^\dagger G(K) = 1 - F(K)$: again this follows from the definitions of $G(K)$ and $F(K)$ and from equation (D.22).

Using these above five results it is found that

$$\begin{aligned} C_L^\dagger C_L &= G(K)^\dagger G(K) + G(K)^\dagger F(K) + F(K)^\dagger G(K) + F(K)^\dagger F(K) \\ &= 1, \end{aligned} \quad (\text{B.2})$$

and similarly for $C_L C_L^\dagger$.

Also since C_L is defined in terms of quasispin operators (equations (4.117)→(4.120)) which are hermitian, it follows that C_L itself is also hermitian, i.e.

$$C_L^\dagger = C_L. \quad (\text{B.3})$$

Combined with the unitary property of C_L it follows that C_L is self-inverse, i.e.

$$C_L = C_L^{-1}. \quad (\text{B.4})$$

B.2 C_L toggles empty/filled states

It will now be proved that C_L toggles empty/filled states where extensive use is made of the basic results:

$$a_K^\dagger n(K) = a_K^\dagger a_K^\dagger a_K = 0, \quad (\text{B.5})$$

$$n(K) a_K^\dagger = (1 - a_K a_K^\dagger) a_K^\dagger = a_K^\dagger, \quad (\text{B.6})$$

$$n(K) a_K = 0, \quad (\text{B.7})$$

$$\text{and } a_K n(K) = a_K. \quad (\text{B.8})$$

Thus:

$$\begin{aligned} F(K) a_K^\dagger &= (n(K)(1 - n(\bar{K})) + n(\bar{K})(1 - n(K))) a_K^\dagger, \\ &= a_K^\dagger (1 - n(K)), \end{aligned} \quad (\text{B.9})$$

$$G(K) a_K^\dagger = \tilde{a}_K (1 - n(K)), \quad (\text{B.10})$$

where the latter holds regardless if $G(K)$ is defined as in equation (4.55) or (4.120) and hence

$$C(K)_A a_K^\dagger = a_K^\dagger (1 - n(\bar{K})) + \tilde{a}_K (1 - n(K)). \quad (\text{B.11})$$

Similarly,

$$a_K F(K) = a_K(1 - n(\bar{K})) \quad (\text{B.12})$$

$$\text{and } a_K G(K) = -(1 - n(K))\tilde{a}_K^\dagger, \quad (\text{B.13})$$

$$\text{thus } a_K C(K)_A = a_K(1 - n(\bar{K})) - \tilde{a}_K^\dagger(1 - n(K)). \quad (\text{B.14})$$

This implies that

$$\tilde{a}_K C(K)_A = a_K^\dagger(1 - n(\bar{K})) + \tilde{a}_K(1 - n(K)) = C(K)_A a_K^\dagger \quad (\text{B.15})$$

and since $C(K)_A = C(\bar{K})_A$ and $[C_{Ai}, C_{Aj}] = 0$ the result follows:

$$C_L a_K^\dagger = \tilde{a}_K C_L \quad (\text{B.16})$$

B.3 The effect of C_L on quasispin

C_L reverses the x and z components of quasispin, the y component, however, remains unaltered. See equations (4.114)→(4.116).

B.4 C_L and ordinary spin commute

C_L commutes with ordinary spin, as it also does with orbital angular momentum. These properties follow since C_L is constructed from quasispin operators (see equations (4.117)→(4.120)), which are defined to be scalar in both spin and orbital angular momentum spaces (see equation (4.73)).

B.5 $|QM_Q\rangle$ has eigenvalues of ± 1 with respect to $(C_L)^2$

In this section the eigenvalue of C_L on an arbitrary half-filled shell is ascertained. From equation (4.112) the action of C_L on a_K^\dagger is

$$C_L a_K^\dagger C_L^{-1} = (K\bar{K})^* a_{\bar{K}} \quad (\text{B.17})$$

giving, upon reapplication

$$C_L^2 a_K^\dagger C_L^{-2} = (K\bar{K})^* (\bar{K}K) a_K^\dagger \quad (\text{B.18})$$

$$= \{K\} a_K^\dagger \quad (\text{B.19})$$

$$= (-a_K^\dagger). \quad (\text{B.20})$$

C_L on an empty shell fills it in the following manner

$$C_L|0\rangle \equiv \left(\prod_K (K\bar{K}) a_K^\dagger a_{\bar{K}}^\dagger\right)|0\rangle \equiv |C\rangle, \quad (\text{B.21})$$

therefore double action of C_L on the empty shell gives

$$C_L^2|0\rangle = C_L|C\rangle \equiv \left(\prod_{K'} (\bar{K}'K')^* a_{\bar{K}'}^\dagger a_{K'}^\dagger\right) \left(\prod_K (K\bar{K}) a_K^\dagger a_{\bar{K}}^\dagger\right)|0\rangle \quad (\text{B.22})$$

$$= \left(\prod_K (\bar{K}K)^* (K\bar{K})\right)|0\rangle \quad (\text{B.23})$$

$$= (-1)^\lambda |0\rangle, \quad (\text{B.24})$$

where λ is the dimension of the irreducible representation the shell transforms as. This implies that for an arbitrarily filled shell of occupancy N

$$C_L^2 (a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger |0\rangle) = (-1)^{\lambda-N} (a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger |0\rangle) \quad (\text{B.25})$$

$$= (-1)^{2M_Q} (a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger |0\rangle) \quad (\text{B.26})$$

since $M_Q = \frac{1}{2}(\lambda - N)$ and

$$Q = \frac{1}{2}(\lambda - \nu), \quad (\text{B.27})$$

where ν is the seniority number. Suppose $N = \nu$ in the example above, then $M_Q = Q$, i.e.

$$C_L^2 |N = \nu\rangle = (-1)^{2Q} |N = \nu\rangle. \quad (\text{B.28})$$

Acting on this state with Q_+ , means adding another *pair* of electrons, this does *not* affect the overall phase of C_L^2 . So

$$C_L^2 |(N-2) = \nu\rangle = (-1)^{2Q} |(N-2) = \nu\rangle, \quad (\text{B.29})$$

which implies that for an arbitrarily filled state labelled with the (composite) label $|K\rangle$

$$C_L^2|K\rangle = (-1)^{2Q}|K\rangle, \quad (\text{B.30})$$

hence the phase of C_L may be fixed to be

$$C_L|QM_QK'\rangle = \pi_Q|Q - M_QK'\rangle \quad (\text{B.31})$$

$$= (Q\bar{Q})|Q - M_QK'\rangle \quad (\text{B.32})$$

$$= (-1)^{Q-M_Q}|Q - M_QK'\rangle. \quad (\text{B.33})$$

The composite label K' now refers to all other labels required to identify the state. The implicit assumption here is that quasispin is compatible with these labels. See §4.1.4.

Appendix C

Proofs of properties of C'_A

C.1 C'_A is unitary

C'_A is unitary because both C_L and T are unitary.

C.2 C'_A toggles empty/filled states

That C'_A toggles empty/filled states is proved by equations (4.146) and (4.147).

C.3 C'_A anticommutes with quasispin

That C'_A anticommutes with quasispin is proved by equations (4.150)→(4.152).

C.4 C'_A and ordinary spin anticommute

C'_A anticommutes with ordinary spin and orbital angular momentum. This follows since C_L commutes, but T anticommutes with \underline{S} and \underline{L} .

C.5 $|QM_Q\rangle$ has eigenvalues of ± 1 with respect to $(C'_A)^2$

$(C'_A)^2$ has eigenvalues of ± 1 follows from the corresponding property for $(C_L)^2$ and the well known result for T^2 (see equation (4.176)).

Appendix D

Proofs of tensor coupling relations

This appendix is a (somewhat detailed) series of proofs of certain coupled-tensor relations discussed in §4.2. A new bracket type has been used here (as in §4.2), “ $\left\langle \right\rangle$ ” and “ $\left\{ \right\}$ ” to indicate that the operators enclosed are tensorially coupled. The right superscripted indices in parentheses indicate from left to right: space/spin rank, quasispin rank. Where pertinent, a right subscript indicates the projection of the superscripted index directly above.

The following relations (D.1 to D.5) will be given proofs:

$$\left\langle A_K, A_L \right\rangle^{(00)} = \delta_{K\bar{L}}(n(\bar{K}) - n(K) - 1)/\sqrt{2} \quad (\text{D.1})$$

$$\left\langle [A_K, A_L] \right\rangle^{(00)} = \sqrt{2}(n(\bar{K}) - n(K)) \quad (\text{D.2})$$

$$\left\{ \{A_K, A_L\} \right\}^{(00)} = -\sqrt{2} \quad (\text{D.3})$$

$$\left\{ [A_K, A_{\bar{K}}] \right\}_{\alpha}^{(01)} = 0 \quad (\text{D.4})$$

$$\left\{ \{A_K, A_{\bar{K}}\} \right\}_{\alpha}^{(01)} = -(2\sqrt{2}i)Q(K)_{\alpha}. \quad (\text{D.5})$$

Relation (D.1) can be shown as follows:

$$\left\langle A_K A_L \right\rangle^{(00)} = (KL)(qq')A_{Kq}A_{Lq'}, \quad (\text{D.6})$$

$$= (KL) \left(a_K^{\dagger} \tilde{a}_L - \tilde{a}_K a_L^{\dagger} \right) / \sqrt{2}, \quad (\text{D.7})$$

$$= \left(-a_K^{\dagger} a_K + a_L^{\dagger} a_L - 1 \right) / \sqrt{2}, \quad (\text{D.8})$$

$$= \delta_{L\bar{K}}(n(\bar{K}) - n(K) - 1)/\sqrt{2}. \quad (\text{D.9})$$

This implies;

$$\left\{ [A_K, A_L] \right\}^{(00)} \equiv \left\{ A_K A_{\bar{K}} \right\}^{(00)} - \left\{ A_{\bar{K}} A_K \right\}^{(00)}, \quad (\text{D.10})$$

$$= (n(\bar{K}) - n(K) - 1)/\sqrt{2} - (n(K) - n(\bar{K}) - 1)/\sqrt{2}, \quad (\text{D.11})$$

$$= \sqrt{2} (n(\bar{K}) - n(K)), \quad (\text{D.12})$$

which is relation (D.2), and also;

$$\left\{ \{A_K, A_L\} \right\}^{(00)} \equiv \left\{ A_K A_L \right\}^{(00)} + \left\{ A_L A_K \right\}^{(00)} \quad (\text{D.13})$$

$$= (n(\bar{K}) - n(K) - 1)/\sqrt{2} + (n(K) - n(\bar{K}) - 1)/\sqrt{2}, \quad (\text{D.14})$$

$$= -\sqrt{2}, \quad (\text{D.15})$$

which is relation (D.3). To prove relations (D.4) and (D.5) it should first be noted that the coupled tensor $\left\{ A_L A_K \right\}_{\alpha}^{(01)}$ is symmetric in K and L , i.e.

$$\left\{ A_L A_K \right\}_{\alpha}^{(01)} = i/\sqrt{2} (LK) \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle A_{Lq} A_{Kq'}, \quad (\text{D.16})$$

$$= i/\sqrt{2} (-(KL)) \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle (-A_{Kq'} A_{Lq} + (KL)(qq')), \quad (\text{D.17})$$

$$= i/\sqrt{2} (KL) \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle A_{Kq'} A_{Lq} - i/\sqrt{2} (qq') \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle, \quad (\text{D.18})$$

$$= \left\{ A_K A_L \right\}_{\alpha}^{(01)}, \quad (\text{D.19})$$

where the last term in the penultimate equation above vanishes as it involves the coupling of a symmetric and an antisymmetric term. Hence relation (D.4) follows and

$$\left\{ \{A_K, A_L\} \right\}_{\alpha}^{(01)} = \left\{ A_K A_L \right\}_{\alpha}^{(01)} + \left\{ A_L A_K \right\}_{\alpha}^{(01)}, \quad (\text{D.20})$$

$$= -(2\sqrt{2}i)Q(K)_{\alpha}, \quad (\text{D.21})$$

because $Q(K)_{\alpha} \equiv i/\sqrt{2} \left\{ A_K A_L \right\}_{\alpha}^{(01)}$, which proves relation (D.5).

D.1 Quasispin tensors coupled to rank 2

Stedman gives the anticommutation relations

$$\{Q(K)_i, Q(K)_j\} = 2\delta_{ij} (Q(K)_Z)^2 \quad (\text{D.22})$$

$$= \delta_{ij} (1 - n(K) - n(\bar{K}) + 2n(K)n(\bar{K}))$$

and states that $\left\{Q(K)Q(K)\right\}_M^{(02)} = 0$ is an equivalent statement. Although Stedman indicates there is no elegant proof to the last theorem it will now be shown to be true:

The proof relies on that fact that

$$\left\{Q(K)Q(K)\right\}_M^{(02)} = Q(K)_\alpha Q(K)_\beta \langle 2M | 1\alpha 1\beta \rangle \quad (\text{D.23})$$

$$= -\frac{1}{2} A_{Kq} A_{\bar{K}q'} A_{Kr} A_{\bar{K}r'} \langle 1\alpha | \frac{1}{2} q \frac{1}{2} q' \rangle \langle 1\beta | \frac{1}{2} r \frac{1}{2} r' \rangle \langle 2M | 1\alpha 1\beta \rangle \quad (\text{D.24})$$

and uses the following information:

- Terms arising from anticommutators of the A_{Kq} in $\left\{Q(K)Q(K)\right\}_M^{(02)}$ must vanish. The A_{Kq} have quasispin magnitude $\frac{1}{2}$ and hence there are two quasispin $\frac{1}{2}$ labels coupled to quasispin 2, which is forbidden.
- When $M \neq 0$ (say $M > 0$) $\left\{Q(K)Q(K)\right\}_M^{(02)}$ must involve two operators with the same labels — which annihilate each other — give 0 — when brought together.
- When $M = 0$ (i.e. $\alpha, \beta = \pm 1$ or $\alpha = \beta = 0$) terms which don't vanish for any other reason given previously come in pairs of products of operators which have the form —

$$A_{K+} A_{\bar{K}+} A_{K-} A_{\bar{K}-}, \quad (\text{D.25})$$

$$A_{K+} A_{\bar{K}-} A_{K-} A_{\bar{K}+} \quad (\text{D.26})$$

— the sum vanishes as the (fermionic) terms are related by an odd number of permutations.

The cases for different values of M will now be considered separately.

$M > 0, M < 0:$

These cases are shown by substituting

$$\{A_{Kq}, A_{Lq'}\} = (LK)(qq') \Rightarrow A_{Kq} A_{Lq'} = A_{Lq'} A_{Kq} + (LK)(qq') \quad (\text{D.27})$$

into equation (D.24). In addition, since $q + q' = \alpha$, $r + r' = \beta$ and $\alpha + \beta = M$, then $M = q + q' + r + r' > 0$ ($= 1, 2$).. But $q, q', r, r' = \frac{1}{2}, -\frac{1}{2}$, hence

$$\underbrace{A_{K+}A_{\bar{K}+}A_{K+}A_{\bar{K}+}, \quad A_{K+}A_{\bar{K}+}A_{K+}A_{\bar{K}-}, \quad \text{and permutations of qspin labels.}}_{\equiv 0} \quad (\text{D.28})$$

Similarly for $M < 0$.

$$\boxed{M = 0:}$$

Expanding equation (D.24) in full gives

$$\left\{ Q(K)Q(K) \right\}_M^{(02)} = -\frac{1}{2} \left(\begin{aligned} & A_{K+}A_{\bar{K}+}A_{K-}A_{\bar{K}-} \langle 11 | \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 1-1 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 20 | 111-1 \rangle \quad (\text{D.29}) \\ & + A_{K-}A_{\bar{K}-}A_{K+}A_{\bar{K}+} \langle 1-1 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 11 | \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 20 | 1-111 \rangle \quad (\text{D.30}) \\ & + A_{K+}A_{\bar{K}-}A_{K+}A_{\bar{K}-} \langle 10 | \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 10 | \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 20 | 1010 \rangle \quad (\text{D.31}) \\ & + A_{K-}A_{\bar{K}+}A_{K-}A_{\bar{K}+} \langle 11 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 10 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 20 | 1010 \rangle \quad (\text{D.32}) \\ & + A_{K-}A_{\bar{K}+}A_{K+}A_{\bar{K}-} \langle 10 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 10 | \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 20 | 1010 \rangle \quad (\text{D.33}) \\ & + A_{K+}A_{\bar{K}-}A_{K-}A_{\bar{K}+} \langle 10 | \frac{1}{2} \frac{1}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle 10 | \frac{1}{2} - \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle \langle 20 | 1010 \rangle \end{aligned} \right). \quad (\text{D.34})$$

The expressions corresponding to (D.29) and (D.30) cancel because the products of the Clebsch-Gordon coefficients is equal, as do those corresponding to (D.33) and (D.34), whereas those corresponding to (D.31) and (D.32) are each identically 0, which exhausts the possibilities.

Appendix E

Proof of quasispin commutation relations

With the $2j$ phase $\{K\}$ set to -1 (see §4.2.2.3) it is possible to examine the commutation relations of the spherical components of quasispin, as defined in §4.2.

The proof that $[Q(K)_1, Q(K)_{-1}] = -iQ(K)_0$ is:

$$[Q(K)_1, Q(K)_{-1}] = \frac{1}{2} [a_K^\dagger a_L^\dagger, a_L a_K] \quad (\text{E.1})$$

$$= \frac{1}{2} \left(a_K^\dagger a_L [a_L^\dagger, a_K] + a_K^\dagger [a_L^\dagger, a_L] a_K + [a_K^\dagger, a_L] a_K a_L^\dagger + a_L [a_K^\dagger, a_K] a_L^\dagger \right) \quad (\text{E.2})$$

$$= \frac{1}{2} (2a_K^\dagger a_L^\dagger a_L a_K - a_K^\dagger a_K + 2a_L a_K^\dagger a_K a_L^\dagger - a_L a_L^\dagger) \quad (\text{E.3})$$

$$= \frac{1}{2} (2a_K^\dagger a_K a_L^\dagger a_L - a_K^\dagger a_K + 2a_K^\dagger a_K a_L a_L^\dagger - a_L a_L^\dagger) \quad (\text{E.4})$$

$$= \frac{1}{2} (a_K^\dagger a_K - a_L a_L^\dagger) \quad (\text{E.5})$$

$$= \frac{1}{2} (a_K^\dagger a_K + a_L^\dagger a_L - 1) \quad (\text{E.6})$$

$$= -iQ(K)_0. \quad (\text{E.7})$$

That

$$[Q(K)_{-1}, Q(K)_0] = \frac{-1}{2\sqrt{2}} (LK)^* \left([a_L a_K, a_L a_L^\dagger] - [a_L a_K, a_K^\dagger a_K] \right) \quad (\text{E.8})$$

and

$$[Q(K)_1, Q(K)_0] = \frac{-1}{2\sqrt{2}}(KL) \left([a_K^\dagger a_L^\dagger, a_L a_L^\dagger] - [a_K^\dagger a_L^\dagger, a_K^\dagger a_K] \right) \quad (\text{E.9})$$

will now also be shown.

Consider the commutation relations of the annihilation and creation operators:

$$\begin{aligned} [a_L a_K, a_L a_L^\dagger] &= a_L [a_K, a_L] a_L^\dagger + [a_L, a_L] a_K a_L^\dagger \\ &\quad + a_L a_L [a_K, a_L^\dagger] + a_L [a_L, a_L^\dagger] a_K \end{aligned} \quad (\text{E.10})$$

$$= a_L (a_L a_L^\dagger - a_L^\dagger a_L) a_K \quad (\text{E.11})$$

$$= a_L (a_L a_L^\dagger - (1 - a_L a_L^\dagger)) a_K \quad (\text{E.12})$$

$$= a_L (2a_L a_L^\dagger - 1) a_K \quad (\text{E.13})$$

$$= -a_L a_K \quad (\text{E.14})$$

and

$$\begin{aligned} [a_L a_K, a_K^\dagger a_K] &= a_L [a_K, a_K^\dagger] a_K + [a_L, a_K^\dagger] a_K a_K \\ &\quad + a_K^\dagger a_L [a_K, a_K] + a_K^\dagger [a_L, a_K] a_K \end{aligned} \quad (\text{E.15})$$

$$= a_L (a_K a_K^\dagger - a_K^\dagger a_K) a_K \quad (\text{E.16})$$

$$= a_L a_K a_K^\dagger a_K \quad (\text{E.17})$$

$$= a_L (1 - a_K^\dagger a_K) a_K \quad (\text{E.18})$$

$$= a_L a_K \quad (\text{E.19})$$

and

$$\begin{aligned} [a_K^\dagger a_L^\dagger, a_L a_L^\dagger] &= a_K^\dagger [a_L^\dagger, a_L] a_L^\dagger + [a_K^\dagger, a_L] a_L^\dagger a_L^\dagger \\ &\quad + a_L a_K^\dagger [a_L^\dagger, a_L^\dagger] + a_L [a_K^\dagger, a_L^\dagger] a_L^\dagger \end{aligned} \quad (\text{E.20})$$

$$= a_K^\dagger a_L^\dagger a_L a_L^\dagger \quad (\text{E.21})$$

$$= a_K^\dagger a_L^\dagger \quad (\text{E.22})$$

and

$$\begin{aligned} [a_K^\dagger a_L^\dagger, a_K^\dagger a_K] &= a_K^\dagger [a_L^\dagger, a_K^\dagger] a_K + [a_K^\dagger, a_K^\dagger] a_L^\dagger a_K \\ &\quad + a_K^\dagger a_K^\dagger [a_L^\dagger, a_K] + a_K^\dagger [a_K^\dagger, a_K] a_L^\dagger \end{aligned} \quad (\text{E.23})$$

$$= a_K^\dagger a_L^\dagger a_K^\dagger a_K + a_K^\dagger (a_K^\dagger a_K - a_K a_K^\dagger) a_L^\dagger \quad (\text{E.24})$$

$$= -(1 - a_K a_K^\dagger) a_K^\dagger a_L^\dagger \quad (\text{E.25})$$

$$= -a_K^\dagger a_L^\dagger. \quad (\text{E.26})$$

These imply that

$$[Q(K)_{-1}, Q(K)_0] = \frac{-1}{2\sqrt{2}}(LK)^*(-a_L a_K - a_L a_K) \quad (\text{E.27})$$

$$= \frac{1}{\sqrt{2}}(LK)^* a_L a_K \quad (\text{E.28})$$

$$= -iQ(K)_{-1} \quad (\text{E.29})$$

and

$$[Q(K)_1, Q(K)_0] = \frac{-1}{2\sqrt{2}}(KL)(a_K^\dagger a_L^\dagger - (-a_K^\dagger a_L^\dagger)) \quad (\text{E.30})$$

$$= \frac{-1}{\sqrt{2}}(KL)a_K^\dagger a_L^\dagger \quad (\text{E.31})$$

$$= iQ(K)_1. \quad (\text{E.32})$$

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